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Contents

Curtis F. Marbut, 1863–1935 345

Chemical Nature of Organic Matter in Different Soil Types. SELMAN A. WAKSMAN AND I. J. HUTCHINGS 347

The Availability of Soil Potassium. JOHN LAMB, JR. 365

A Simple Method of Estimating Exchangeable Calcium and Other Bases in Non-Calcareous Soils. AMAR NATH PURI 383

A Device for Measuring Precipitation Waters Lost from the Soil as Surface Runoff, Percolation, Evaporation, and Transpiration. G. W. MUSGRAVE. 391

Sorption of Liquids by Soil Colloids: II. Surface Behavior in the Hydration of Clays. L. D. BAVER AND HANS WINTERKORN 403

John Sharkey Carroll, 1871–1935 421

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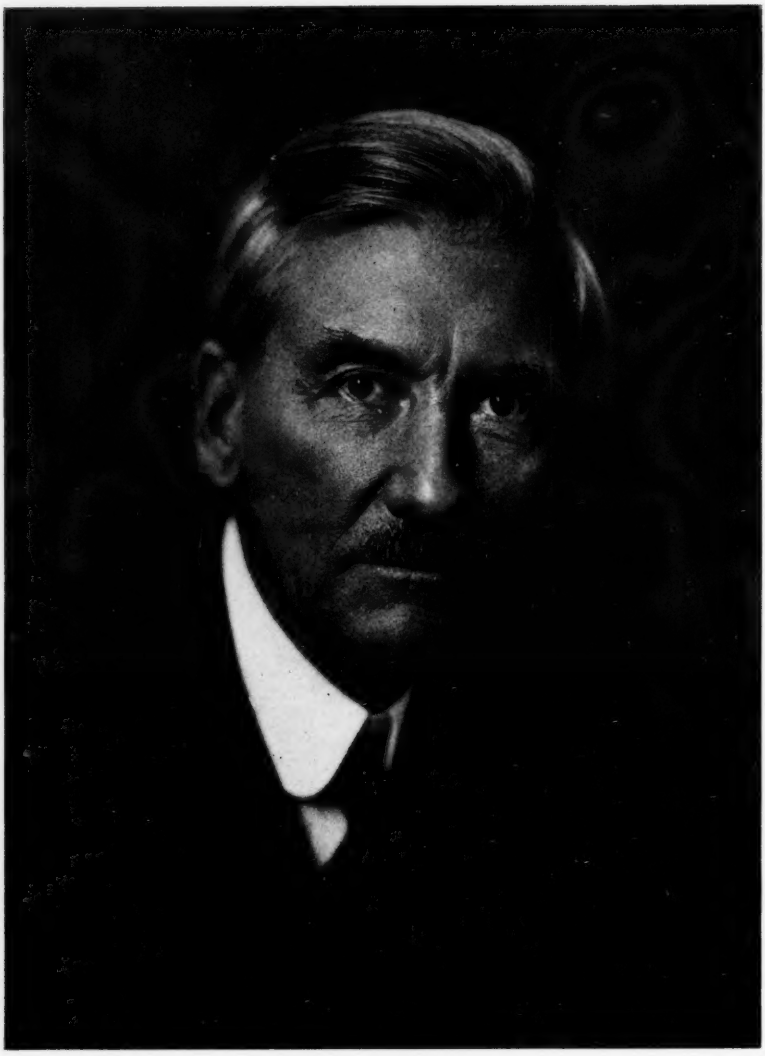

CURTIS F. MARBUT

Curtis F. Marbut
1863–1935

One of the world's greatest authorities on soils, Dr. Curtis F. Marbut, for many years Chief of the Soil Survey of the United States Department of Agriculture, died in Harbin, Manchuria, August 25. At the time of his death, he was on his way to make a study of the soils of China at the request of the Chinese Government.

Doctor Marbut, who had passed the age of retirement, had been retained by the United States Government for two additional years in order to continue exceptionally important research on the classification of soils in this and other countries.

For twenty-five years Doctor Marbut had supervision of the soil survey work of the United States Department of Agriculture, which has mapped approximately one billion acres of land, or about half the agricultural area of the United States. He recently finished the first complete inventory of the soil resources of the entire nation. This volume, soon to be published by the United States Department of Agriculture as part three of its *Atlas of American Agriculture*, contains the information accumulated during his supervision of the Soil Survey, and its mapping and description of the soils of 1,500 counties and areas in the United States and its insular possessions. As a guide to farm practice, this inventory of soil resources is becoming established as one of the most important parts in the scientific foundation of this country's agricultural program.

Not only did Doctor Marbut know the soils of the United States, but he had examined and classified the soils in every country of western Europe, except Spain. He was familiar with the soils of Russia, had directed the classification of the soils of Africa, and had made a study of the soils of South America.

In recognition of his extensive studies and classification of soils, which have furnished an important contribution to the soil geography of the world, Doctor Marbut was awarded the Cullum Geographical Medal in 1930, "for services of special distinction in the field of exploration and geographic research." He received the degree of doctor of laws from the University of Missouri, from which he was graduated in 1889, and where he was formerly professor of geology. He also received the degree of doctor of science from Rutgers University. He was chairman of the International Commission on Genesis, Classification, Morphology, and Mapping of Soils and was president of Commission V on Soil Classification at the Third International Congress of Soil Science at Oxford, England, where during the first week of August he presided over important discussions by members of the congress from all parts of the world. Doctor Marbut was a member of many learned societies. He was born in Lawrence County, Missouri, July 19, 1863.

CHEMICAL NATURE OF ORGANIC MATTER IN DIFFERENT SOIL TYPES[1]

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A systematic study of the proximate chemical composition of the organic matter or humus in composts (19), peats (21), and the upper layers of forest soils (23) represents comparatively little difficulty, largely because of the fact that these formations are predominantly organic in nature. One can readily establish the relation between the specific chemical constituents of these types of humus and the corresponding compounds in the plant residues from which these humus formations originated. The study of humus in soil horizons which are predominantly inorganic in nature, however, represents a number of highly confusing problems. The great majority of investigations carried out with this type of humus were based upon preparations obtained from mineral soils by means of strong chemical reagents, which resulted in considerable changes in the chemical nature of the humus. There was still less justification for applying data obtained from the study of humus in peats and even coals to an understanding of the chemical composition of humus in field and garden soils. The chemistry of humus in mineral soils, its function, and its transformations still represent a number of unsolved problems which are among the most important in soil science.

The very conception of humus has recently been subjected to considerable criticism. Sufficient emphasis has already been laid (16, 17) upon the fact that humus in not—*1*, the alkali-soluble portion of the soil organic matter; nor *2*, the alkali-soluble and acid-precipitated portion; nor *3*, that fraction of the soil which is oxidized by dilute H_2O_2 or by other mild oxidizing agents; nor *4*, the acetyl-bromide insoluble portion; nor *5*, any other fraction of the organic matter. It represents the total organic matter of the soil and must be considered as such. It has been definitely established that humus does not consist of a few simple compounds, the so-called humic acids, to which various hypothetical formulas have been ascribed, but that it is highly complex in chemical composition. It has been further suggested (16, 22) that

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

[2] The authors are indebted to Prof. A. W. Blair, to Dr. Marbut, and to Dr. Shaw, for supplying samples of soil, and to Dr. M. C. Allen, formerly of this laboratory, for assistance in some of the analyses.

humus be divided, by the method of proximate analysis, into several groups of organic complexes possessing definite chemical properties and having their corresponding constituents in plant residues.

The study of humus in mineral soils presents a number of problems dealing, aside from its chemical nature, also with its formation; transformation by microörganisms and chemical agencies; functions in soil processes, especially its relation to the physical and chemical properties of the soil; and soil fertility. Most significant of these are two problems, based upon the quantitative and qualitative composition of humus, which involve a study of methods for determining the abundance and chemical nature of humus in mineral soils. These form the subject of this paper.

QUANTITATIVE DETERMINATION OF ORGANIC MATTER IN MINERAL SOILS

The more important methods proposed at different times for determining the organic matter content of mineral soils can be divided into the following four groups: 1. loss on ignition, directly, or after preliminary treatment of the soil with certain chemical reagents so as to remove those mineral complexes which may also give a loss on ignition; 2. complete combustion of the organic matter and calculation of the total humus from the organic carbon content, by the use of a certain arbitrary factor; 3. oxidation of humus by means of strong oxidizing agents; 4. miscellaneous other methods, such as calculation of humus from the total nitrogen in the soil and the distillation method. A number of methods have also been proposed for determining the abundance in soil of certain humus fractions, usually designated as the "humified" portions of the soil organic matter. The assumption was thereby made that plant and animal substances, in the process of their decomposition, change first into humus before they become completely mineralized. Aside from the lack of validity for any such assumption, these methods need not be discussed here further, since they have only a limited bearing upon the problem under consideration.

Ignition methods.—It has been definitely agreed that the loss-on-ignition method cannot be recommended for determining accurately the organic matter content of mineral soils. The error involved by the use of this procedure is too large to make the results more than highly proximate in nature. This method was modified by Rather (8), who suggested treatment of the soil, previous to ignition, with a mixture of dilute hydrochloric and hydrofluoric acids. This modification suffers from certain distinct disadvantages: 1. some of the constituents of the humus, such as the uronic acid complexes, tend to be destroyed during the preliminary treatment of the soil, while other humus fractions may be brought into solution; 2. the method is time consuming (1); 3. at best, the results thus obtained are only indirect.

Combustion methods.—The complete oxidation of the soil organic matter, whether by dry or wet combustion methods, has been used most extensively.

It is now generally agreed that the determination of the total organic carbon in soil is the most accurate method available, at the present time, for determining the humus content. However, certain difficulties arise in interpreting the results thus obtained, chief among which is the specific factor to be used for calculating the humus from the carbon data. Fresh plant residues contain about 50 per cent carbon, thus giving a ratio of organic matter (a very low ash content being assumed) to carbon of about 2:1. When these residues are allowed to undergo decomposition by microörganisms in soils or in composts, the carbon content of the resulting humus becomes gradually higher, but never above 60 per cent unless the residues become fossilized. This is due to the fact that the carbohydrate constituents of the plants, namely, the sugars, polyuronides, hemicelluloses, and cellulose, which have a carbon content of 38 to 43 per cent, are among the first to decompose and disappear from the humus. On the other hand, the lignin, with a carbon content of 62–64 per cent is more resistant to decomposition and, therefore, accumulates. The proteins with a carbon content of 50–52 per cent also tend to persist in the humus and even accumulate.

The carbon content of the humus which results from the decomposition of the plant and animal residues depends largely upon the extent of their decomposition. In the case of the upper layers of a raw humus forest soil or of a highmoor peat bog, the carbon content increases only little, perhaps only to 52 or 54 per cent, because of the persistence of a large part of the carbohydrates. When humus is at that stage of decomposition when most of the cellulose and hemicelluloses have disappeared, the carbon content will have increased to 56 and even 58 per cent, as is the case in mineral soils, lowmoor and sedimentary peats, and the lower horizons of forest soils. This bears out fully the earlier ideas of Wolff (26), van Bemmelen (2), and others who assumed that the carbon content of humus is 58 per cent and that the factor to be used for calculating the amount of humus in mineral soils should be 1.724. In the case of the humus horizons of forest (7), heath, and alpine soils, however, this factor has to be modified, since the humus in these soils contains a considerable amount of cellulose and hemicelluloses; in the case of the upper layers of forest soils, peat bogs, and peat soils, the determination of the organic matter content by the loss on ignition is frequently justified.

Oxidation methods.—Among the various oxidation methods, that of Robinson (10), which consists in the treatment of soil with 15 to 30 per cent hydrogen peroxide, deserves particular attention; however, this method as well has been shown (1) to be far from satisfactory. The permanganate method of Istsherikov, the sodium peroxide method of Parr, and other oxidation procedures are also open to criticism, on various grounds which need not be discussed here.

Among the rapid methods of humus determination in soil, the Schollenberger (12) procedure or one of its modifications (15) deserves careful consideration.

The results obtained by this method check very well with those obtained by complete combustion, even in the case of soils of a very low organic matter content.

Other methods.—In many cases, the humus content of the soil was calculated from the total nitrogen, as determined by the Kjeldahl method. The relation between organic matter and nitrogen was usually assumed to be 20:1. This method meets with even more serious objections; it involves not only the use of an arbitrary factor, which may vary considerably for different humus formations, but it also assumes a constant relation between the carbon and nitrogen content of the humus. This method as well cannot, therefore, be recommended.

TABLE 1

Organic matter content of a series of soils, as determined by different methods

Per cent of air-dry material

NAME OF SOIL	ORGANIC MATTER BY DISTILLATION METHOD*	CARBON CONTENT BY COMBUSTION METHOD	CARBON BY OXIDATION METHOD (MODIFICATION OF SCHOLLENBERGER METHOD)	ORGANIC MATTER BY COMBUSTION METHOD (C × 1.724)	NITROGEN CONTENT
Michigan podzol, 3.5–5 cm	33.19	24.11	25.26	41.47	1.07
Michigan podzol, 5–20 cm	0.71	0.65	0.64	1.12	0.052
Tchernozem soil, Texhoma, Okla., 0–20 cm	1.43	0.78	0.82	1.41	0.086
Tchernozem soil, Texhoma, Okla., 20–50 cm	1.31	0.60	0.64	1.10	0.073
Chestnut soil, N. M. 0–18 cm	1.08	0.95	1.09	1.93	0.101
Serozem, Ariz., 0–15 cm	0.37	0.16	0.16	0.28	0.023
Colbert clay, 0–15 cm	0.50	0.67	0.64	1.16	0.048
Hagerstown clay, 50–75 cm	0	0.18	0.31	0.31	0.037
Stockton adobe, 0–40 cm	0.40	0.53	0.60	0.91	0.051
Irredell loam, 30–40 cm	0.26	0.30	0.38	0.52	0.042
Marion silt loam, surface	2.44	1.80	1.70	3.10	0.170

* Analyses made by Dr. Bouyoucos.

Bouyoucos (4) suggested that the organic matter content of the soil be calculated by determining both the loss on ignition and the amount of chemically combined water. Air-dried soil was heated at a high temperature and the liberated water condensed; the weight of this water was subtracted from the loss on ignition, to give the amount of organic matter present. This method has no advantage over the other methods already referred to, especially since it is more complicated and less direct. The organic matter in a series of soils analyzed by Bouyoucos was compared with the amount of humus found in these soils by the combustion method (table 1). The distillation procedure gave in most cases too low results, frequently less than a half of the organic matter content of the soil, as calculated from the organic carbon.

A comparison of the different methods for the determination of humus in mineral soils can lead to only one conclusion, namely, that the only reliable method available at the present time is that based upon the organic carbon content. All other methods are either proximate in nature or more complicated, and usually less reliable. The major difficulty involved in the use of this method is the nature of the factor used in calculating the humus. Because of the undisputed fact that the carbon content of the organic matter in composts, peat bogs, and mineral soils varies, depending on the extent of its decomposition, the use of any one factor has frequently been questioned. It has even been suggested (7) that different factors be used for different types of humus. However, since even one type of humus varies considerably, depending on a number of factors, especially the nature of the residues undergoing decomposition, the mineral part of the soil, the type of decomposition, and the extent of decomposition, one has to exercise special precautions in recommending the use of several factors. If any multiplicity of factors is to be recommended, the following deserve consideration:

The factor 1.724, proposed by Wolff and used extensively by soil chemists and geneticists, for mineral soils.

The factor 1.862, for lowmoor and sedimentary peats and for the F and H layers of raw-humus forest and heath soils.

The factor 2.0 for composts, highmoor or sphagnum peats, and litter of forest soils.

If the mineral content of a particular soil layer, such as the organic layers of forest soils, or of other humus formation, such as peats and composts, is less than 10 per cent, the loss on ignition is as reliable as the foregoing method of calculation.

CHEMICAL NATURE OF HUMUS IN MINERAL SOILS

Three distinctly different methods of approach have been utilized for the study of the chemical nature of humus in mineral soils: 1. The separation of the humus into several groups of complexes by extraction with dilute alkali solutions and precipitation with acids; whatever justification the study of "humic acids," "humic matter," or "pure humus" may have had from the point of view of the presence in the soil of certain characteristic dark colored, amorphous bodies, high in carbon, it has contributed comparatively little toward an understanding of the chemistry of humus as a whole, its origin, and its rôle in soil processes. 2. The isolation from soil of well-defined chemical compounds of an organic nature; the information thus gained has been of considerable importance for a better understanding of the origin and occurrence of specific complexes in the soil, but it has not explained the chemical nature of humus as a whole. 3. The proximate chemical analysis of humus; just as in the case of natural formations predominantly organic in nature, such as peats and organic layers of forest soils, the humus of mineral soils can be

subdivided into several fractions, characterized by specific chemical properties, which have their counterpart in the plant residues (16, 22).

The proximate method of analysis of humus in mineral soils has now been carried out in various laboratories, so that sufficient evidence has accumulated to determine the extent to which it can be utilized for the study of the organic chemistry of the soil. Unfortunately, certain discrepancies have frequently been introduced by some workers who have attempted to use this method; attention must be called to some of these here. Briefly, the analysis is carried out as follows: one hundred to one thousand gram portions of air-dried soil are treated thoroughly with (a) ether, (b) hot alcohol, (c) hot water, (d) hot 2 per cent HCl solution, and (e) 80 per cent sulfuric acid in the cold. There is little difficulty in determining the amount and nature of the organic matter fractions in the first three extractions. The fraction hydrolyzed by the dilute mineral acid needs further elucidation. The hemicelluloses form the major group of organic constituents of the humus hydrolyzed or brought into solution by this treatment; the total amount of hemicelluloses can be calculated from the reducing substance found in the extract, after the latter has been neutralized with an alkali solution and the inorganic precipitate has been removed by filtration. However, polyuronides are present abundantly in humus; they are also hydrolyzed to a large extent by the dilute acid treatment but are only partly transformed into reducing bodies; the total amount of reducing sugar obtained does not represent, therefore, all the hemicelluloses, including the polyuronides present in the humus. This is largely the reason why the hemicellulose content of humus in mineral soils, especially in gray desert soils, has frequently been reported as too low; this fraction was found abundantly only in the organic layers of podzols, in peats, and in composts. Because of the small amount of reducing sugar found in the dilute acid hydrolyzate of mineral soils and because of the difficulty of determining reducing sugar in low concentrations, some investigators (5) analyzed the hydrolyzate for total carbon and calculated the whole fraction as hemicellulose; the error thus introduced is very large and totally unjustified. A large part of the organic matter in the acid extract is due to hydrolyzed proteins; some is due to lignin, as well as to other complexes brought into solution by the acid; only a part of the hydrolyzate is due to true hemicelluloses. The only justified term for this mixed fraction is "dilute acid hydrolyzable organic fraction;" the hydrolyzed protein must, however, be accounted for, if the protein is reported separately. After hydrolysis with dilute mineral acid, the soil is washed with water and dried, and definite portions (10–15 gm.) are treated with 80 per cent sulfuric acid for the determination of the cellulose and lignin fractions.

This system of analysis can be utilized in numerous investigations of the chemical nature of humus. It is sufficient to mention the study of the degree of decomposition of the humus, especially in peats and in composts. In the case of humus in mineral soils, it can find special application in the study of the influence of soil treatment in modifying the nature of the humus, and in the study of humus in different soil types and in the different horizons of the same soil type.

Influence of soil treatment upon the chemical composition of the humus. For this study, a series of plot and cylinder experiments at the College Farm of the New Jersey Agricultural Experiment Station have been utilized. The special treatment of the plots was carried out for a period of 25 years, so that marked differences were brought about in the chemical nature of the soil as a whole and of the humus content in particular. The cylinder experiments were of shorter duration, hence the modifications of the humus are not so striking.

The results presented in tables 2 and 3 show that the humus content of a given soil type can be considerably modified by treatment; however, the general chemical nature of the humus in the soil tends to be the same. Treatment of the soil plots with stable manure for a period of 25 years resulted in a considerable increase in the humus content, without modifying to any great extent its chemical nature. Liming of the soil brought about a decrease in the ether-soluble fraction and an increase in the water-soluble fraction, but not of the other humus constituents. In the cylinder experiments, the increasing addition of straw resulted in a gradual increase in humus content.

TABLE 2

*Influence of soil treatment upon the chemical nature of humus in a mineral soil**

PLOT NUMBER	7A	5A	19A	7B	5B	19B
TREATMENT†	Untreated	Manure + minerals	Minerals only	Lime	Manure + lime + minerals	Lime + minerals
	Per cent of dry material					
pH	4.6	5.2	5.0	7.4	7.1	7.3
C:N	10.5	11.7	11.2	10.5	10.4	10.8
Organic matter (C × 1.72)	1.41	3.01	1.96	1.74	2.94	1.63
Total nitrogen	0.078	0.149	0.102	0.096	0.165	0.088
	Per cent of total humus					
Ether-soluble portion	5.67	1.53	6.89	0.74	0.82	3.61
Alcohol-soluble portion	1.78	1.57	1.84	1.84	1.49	2.70
Cold- and hot-water-soluble portions	1.84	2.50	2.35	3.58	4.42	3.87
Hemicelluloses	7.19	7.87	7.48	6.05	8.39	6.91
Cellulose	3.64	3.15	2.43	2.45	3.80	2.60
Lignin	34.90	42.20	30.03	34.52	40.71	38.87
Protein	34.61	31.03	32.55	34.48	35.07	33.74
Total accounted for	89.61	89.85	83.57	83.66	94.70	92.30

* Sassafrass loam.

† A detailed discussion of the treatment of these plots for a period of 25 years and crop yields are given by Lipman and Blair (6).

The most important modification of the humus was the gradual decrease in protein content, which, in the case of the soil receiving nitrogen, became marked only with the largest additions of straw. Accompanying the decrease of protein, there was a gradual increase in cellulose. Before any general conclusions are drawn from these experiments, a greater number of analyses will have to be made than was so far possible.

Chemical composition of humus in podzols. The rôle of humus in the process of podzolization is well established and need not be discussed here further. However, although it is known that humus is removed from the A horizon

TABLE 3

*Influence of increasing additions of straw upon the organic matter content of the soil**

CYLINDER NO.	121–2†	123–4	125–6	127–8	129–30	131–2	133–4	135–6	137–8	139–140
STRAW ADDED TONS PER ACRE	0	1	2	4	8	0	1	2	4	8
					Per cent of dry material					
Organic matter (C × 1.724)	2.29	2.36	2.47	2.69	3.26	2.21	2.26	2.40	2.45	3.07
Total nitrogen	0.099	0.102	0.104	0.111	0.126	0.097	0.097	0.107	0.107	0.119
C:N	13.4	13.4	13.6	14.1	15.0	13.2	13.5	13.0	13.3	15.0
Increase in organic matter due to treatment, *per cent*	.....	3.1	7.9	17.5	42.4	.....	2.3	8.6	10.9	38.9
					Per cent of total humus					
Ether-soluble portion	1.2	1.1	1.1	1.2	1.2	1.5	1.4	1.4	1.3	1.4
Alcohol-soluble portion	1.2	1.3	1.3	1.0	0.8	0.7	0.8	0.9	0.9	0.9
Hot-water-soluble portion	1.6	0.9	1.0	0.8	1.2	1.6	1.2	1.1	1.3	1.1
Hemicelluloses	5.2	4.9	5.6	6.0	5.8	3.9	4.3	4.6	5.3	4.5
Cellulose	2.3	3.2	3.6	4.2	3.7	2.4	3.0	2.3	3.7	4.3
Lignin	51.3	50.5	41.9	47.1	57.7	50.8	49.7	43.0	44.3	53.7
Protein	27.0	27.0	26.3	25.8	24.2	27.4	26.8	27.9	27.3	24.2
Total accounted for	89.8	88.9	80.8	86.1	94.6	88.3	87.2	81.2	84.1	90.1

* A detailed discussion of the treatment of these cylinders for a period of 10 years is given by Blair and Prince (3).

† Cylinders 121–130 received, at irregular intervals, extra applications of nitrogen as $NaNO_3$, although cylinders 131–140, as well, had leguminous crops and some nitrogen application.

and is reprecipitated in the B horizon, it still remains to be determined whether this removal takes place at the expense of the humus as a whole or of only certain specific humus constituents. The fact that the nitrogen content of the humus was often found to increase with depth of profile suggests that the latter assumption is justified. It is sufficient to call attention, among the recent investigations, to the work of Weis (25). The following amounts of humus and total nitrogen were found on an average of 10 profiles of Danish heath soils:

HORIZON	HUMUS CONTENT OF SOIL	NITROGEN CONTENT OF SOIL	NITROGEN IN HUMUS
	per cent	*per cent*	*per cent*
Raw humus (A_1)	27.03 (7.98–51.73)	0.49 (0.14 –1.06)	1.81
Bleached sand (A_2)	1.78 (1.05– 2.94)	0.03 (0.02 –0.04)	1.69
Humus hardpan (A_3-B_1)	12.65 (9.85–16.17)	0.29 (0.21 –0.39)	2.29
Iron hardpan (B_2)	2.65 (1.31– 4.66)	0.06 (0.03 –0.10)	2.27
Subsoil (C)	0.24 (0.11– 0.81)	0.005 (0.003–0.016)	2.08

Even larger increases in the relative nitrogen content of the humus, with an increase in depth, were reported in some of his earlier analyses of the profiles of the hill islands and heath plains of Denmark (24).

In order to determine whether there is any difference in the chemical nature of the humus in the various horizons of the podzol profile, the results of analyses of three profiles are reported here (tables 4–6).

The first profile was obtained from a virgin heath on the Clason estate in Jutland, during the summer of 1933. The sample of the A_1 horizon was taken at a depth of 5–8 cm., just below the vegetation layer; that of the A_2 horizon, at a depth of 12–15 cm.; and that of the B horizon, at a depth of 30 cm.

The proximate method of analysis has been modified in the case of these profiles in one important respect. It was found that on treating the material with hot dilute HCl, to determine the hemicelluloses, as well as in the sulfuric acid treatment for the cellulose determination, a considerable amount of the lignin passes through the paper in the water used for washing the hydrolyzed residue; this held true for all the podzol horizons, but especially for the B horizon. The lignin fraction of the humus in this horizon was so mobile that nearly two-thirds of it was removed in the wash water following the acid treatments. In order to account for this lignin, the filtrates were analyzed for total organic carbon; the carbon equivalent of the hemicellulose and cellulose found in the extracts and the carbon equivalent of the hydrolyzed protein were subtracted and the rest of the carbon was calculated as lignin.

The second podzol profile was supplied by Doctor Marbut of the U. S. Department of Agriculture. It represents a trenary sandy loam, from Alge Co., Michigan. Only the A_1 and A_2 horizons of this profile were available, the A_1 being taken at 3–5 cm. and A_2 at 5–20 cm. depth.

The third profile was obtained from a raw-humus forest soil, in a white pine-hemlock forest, at Keene, New Hampshire.

The three podzol profiles varied markedly from one another. Although the first two profiles contained nearly the same amounts of organic matter in the A_1 and A_2 horizons, the nature of this organic matter was quite different. The humus in the heath profile was lower in nitrogen than that of the Michigan podzol, as a result of which the C:N ratio was much wider in the former. The humus in both profiles was high in cellulose, hemicellulose, and lignin in the A_1 horizon; these diminished gradually in the A_2 horizon, accompanied by an increase in the protein content. The ether-soluble substances were high in the heath and low in the Michigan profile; there was an increase in concentration of this fraction from the A_1 to the A_2 horizon, followed by a rapid drop in the B horizon. The results obtained for the third profile were similar to those for the first two profiles. In this case, the litter and A_0 were also analyzed. With an increase in depth, the litter was gradually transformed into typical humus. This process of transformation was characterized by a gradual decrease in the ether-soluble material, in the hemicelluloses, and in the cellulose, and by an increase in the lignin and protein content.

TABLE 4

Chemical composition of humus in a heath podzol

HORIZON	A_1	A_2	B
	Per cent of dry material		
Total humus (C × 1.724)	38.70	1.22	2.99
Total nitrogen	0.54	0.019	0.048
C:N	41.7	37.4	36.3
Nitrogen in humus	1.395	1.557	1.605
	Per cent of humus		
Ether-soluble portion	3.77	13.93	1.32
Alcohol-soluble portion	4.03	3.52	2.75
Cold- and hot-water-soluble portions	0.59	1.14	0.58
Hemicelluloses (sugar × 0.9)	14.25	5.90	8.12
Cellulose (sugar × 0.9)	14.81	5.41	3.12
Lignin, nitrogen-free	50.85	45.74	63.14
Protein	8.71	9.75	10.03
Total accounted for	97.01	85.29	89.06

Although the results of these analyses permit certain generalizations concerning the chemical nature of humus in the podzol profile, they are not sufficient to justify any broad conclusions, because of the important differences in the nature of the profiles. Weis also obtained considerable variation in the chemical composition of different heath podzols, as shown by the variation in nitrogen content and in the C:N ratio.

TABLE 5

Chemical composition of humus in a Michigan podzol

HORIZON	A_1	A_2
	Per cent of dry material	
pH	4.59	5.13
Total humus (C × 1.724)	41.57	1.10
Total nitrogen	1.07	0.052
C:N	22.5	12.4
Nitrogen in humus	2.574	4.727
	Per cent of humus	
Ether-soluble portion	0.97	2.90
Alcohol-soluble portion	2.32	1.68
Cold- and hot-water-soluble portions	4.00	6.36
Hemicelluloses (sugar × 0.9)	11.54	8.18
Cellulose (sugar × 0.9)	5.00	2.10
Lignin, nitrogen-free	55.62	46.32
Protein	16.08	27.82
Total accounted for	95.53	95.36

TABLE 6

Chemical composition of humus in a raw-humus forest podzol

HORIZON	LITTER	F-LAYER	H-LAYER	A_1	A_2	B_1	B_2-C
			Per cent of dry material				
pH	4.5	4.2	3.8	4.0	4.0	4.2	4.3
Loss on ignition, per cent	96.00	82.04	75.20	18.95	5.80	11.75	9.90
C:N	59.5	24.7	26.6	24.6	16.3	18.3	21.8
Organic matter, (C × factor)*	96.17	78.19	74.20	18.46	4.33	8.36	5.94
Total nitrogen	0.84	1.75	1.56	0.42	0.15	0.26	0.15
Nitrogen in humus	0.87	2.24	2.10	2.28	3.46	3.11	2.53
			Per cent of humus				
Ether-soluble portion	6.38	4.86	4.25	3.21	3.12	1.54	1.00
Alcohol-soluble portion	2.57	4.16	3.54	2.25	2.42	1.08	0.98
Cold- and hot-water-soluble portions	4.06	6.73	3.31	1.88	4.10	2.38	1.03
Hemicelluloses	18.23	11.94	9.49	8.00	10.30	8.70	6.22
Cellulose	15.72	8.24	4.75	.....	.....	.....	.....
Lignin	38.38	44.24	50.13	.....	.....	.....	.....
Protein	5.44	14.00	13.12	14.25	21.50	19.43	15.81
Total accounted for	91.65	90.17	85.22	.....	.....	.....	.....

* The factor used for this calculation was (1.684 + 0.004 × C:N).

Chemical composition of humus in tchernozems. The transition of the podzols to the tchernozems is a result of a number of factors, chief among which is the change in climate from the cooler to the warmer regions, a decrease in humidity and rainfall, and a change in type of vegetation. These changes are principally responsible for the difference in the chemical nature of the humus in the two soil types; this is specifically due to (a) differences in the chemical composition of the plant residues, (b) differences in the physical and chemical soil conditions, (c) the specific microbiological population. The abundance of bases (calcium and magnesium) in the tchernozem soil brings

TABLE 7

Chemical composition of the humus in tchernozem soils

NATURE OF SOIL	TEXHOMA, OKLAHOMA	TEXHOMA, OKLAHOMA	AMARILLO, TEXAS	TUANAH, TEXAS	
Per cent of dry material					
Depth, *cm.*	0–20	20–50	Surface	0–20	30–50
pH of soil	6.82	7.01	6.85	7.70	8.05
Total humus (C × 1.724)	1.41	1.10	2.29	2.06	1.58
Total nitrogen	0.086	0.073	0.130	0.149	0.102
C:N	9.5:1	8.8:1	10.2:1	8.0:1	9.0:1
Nitrogen in humus	6.100	6.636	5.677	7.23	6.45
Per cent of humus					
Ether-soluble portion	1.70	3.14	1.57	2.02	2.47
Alcohol-soluble portion	0.90	0.86	0.46	0.74	0.69
Cold- and hot-water-soluble portions	2.76	2.36	2.36	1.32*	0.87*
Hemicelluloses	6.95	3.45	6.72	1.41	0
Cellulose	8.86	4.23	7.16	5.44	4.28
Lignin	32.59	35.26	35.81	35.36	32.53
Protein	38.08	41.45	35.50	44.34	32.53
Total accounted for	91.84	90.75	89.58	90.63	80.84

* Cold-water-soluble only.

about a fixation of the humus which is produced in the decomposition of the plant residues. One would, therefore, expect that a transition from the podzols to the tchernozems should result, not so much in a change in the amount of humus found in these soil types, but rather in a change in its chemical nature.

Remezov (10) found the widest carbon-nitrogen ratio (10:1 to 14:1) in the humus of the tchernozems; this was explained by the higher lignin content, which was 2 to 2.5 times as high as the protein in the humus. These results would seem to conflict with those reported from this laboratory (16), namely, that the humus in tchernozems contains about 41 to 49 per cent lignin-like material and 30 to 35 per cent protein. Remezov, however, subtracted the

nitrogen found in the humus in the form of amides and amino acids from the total nitrogen and calculated the differences as protein, whereas the writer based the calculation of the protein upon the total organic nitrogen. Otherwise, the composition of the humus in the two groups of tchernozems is similar, as regards both protein and lignin concentration.

The results of analyses of three tchernozems—one from Texhoma, Oklahoma; one representing an Amarillo silty clay loam from Texas; and one from Tuanah, Texas—are given in table 7. A very decided difference was found in the chemical nature of the humus in these soils from that in the podzols. The humus in the tchernozems was characterized by a lower lignin and a higher protein content, a much lower hemicellulose and cellulose content, and a narrower C:N ratio. The organic matter in the podzols was not sufficiently decomposed, as shown by the high cellulose and hemicellulose content. This also accounts for the low nitrogen concentration in the humus of the podzols; the lignin seems to accumulate in the humus of these soils, whereas the protein does not accumulate or is partly removed. In the case of the tchernozems, the greater degree of decomposition of the humus, as shown by the low cellulose and hemicellulose content, resulted in a more extensive synthesis of protein; the latter became fixed by the lignin, in the presence of sufficient bases.

The results presented here fully confirm those obtained by Remezov (10) for the humus in the tchernozems; however, they are in total disagreement when the podzols are compared. Possibly, Remezov used, not virgin soils, but cultivated podzols, in which considerable disintegration of some of the humus constituents has taken place.

Chemical composition of humus in chestnut soils and serozems. The narrowest C:N ratio has usually been reported (9) for the humus of serozems (4.5:1), followed by that of the chestnut soils (6.8:1). This was explained by the fact that under the specific conditions of formation of these soils (dry continental climate, hot summer temperature, continuous winds, intensive evaporation and drying of soil), the limited vegetation yields a small amount of residual material which is rapidly decomposed. As a result of this, the humus content of the serozems (0.5–1.5 per cent) is low in spite of the old age of these soils. The humus of serozems was further characterized (10) by a complete absence of both cellulose and hemicelluloses and by a high protein content; the former was ascribed to the extensive decomposition of the plant residues in these soils and the latter to the fact that this humus is chiefly of microbial origin. The low content of lignin complexes was believed to be responsible for the low concentration of absorbed cations and the lack of structure in these soils. Humus in chestnut soils was also characterized by a lack of cellulose but it was high in hemicellulose; the lignin content was greater and the protein content lower than in the previous group of soils.

In the analyses reported here, two serozems and one chestnut soil were used. The latter came from New Mexico, 32 miles south of Tucumcari, and the former came from the Mohave desert, near Tucson, Arizona, and from

the Imperial Valley, California. The results (table 8) show that humus in chestnut soils is very similar in chemical composition to that of tchernozems, especially the humus in the Amarilla soil; the latter can actually be classified as a chestnut soil. There is no marked distinction in chemical composition of the humus in the two soil types, as found by Remezov; there is no abnormally high hemicellulose content in the chestnut soil, and the protein and lignin contents are similar in both soils. Perhaps the difference in the two sets of results is due to a lack of sharp distinction between the two soil types.

The humus in the serozems is quite characteristic. It has a narrow carbon-nitrogen ratio, much narrower than in the other soil types discussed in the

TABLE 8

Chemical composition of the humus in chestnut soil and serozems

NATURE OF SOIL	CHESTNUT	CHESTNUT	ARIZONA SEROZEM	IMPERIAL SEROZEM
Per cent of dry material				
Depth, *cm.*	0–15	15–48	0–15	0–15
pH of soil	6.82	7.01	7.21	8.38
Total humus (C × 1.724)	1.93	1.31	0.28	0.066
Total nitrogen	0.101	0.076	0.0225	0.0064
C:N	11.1:1	10.0:1	6.4:1	6.0:1
Nitrogen in humus	5.233	5.802	8.036	9.697
Per cent of humus				
Ether-soluble portion	2.05	3.13	4.77	1.60
Alcohol-soluble portion	1.09	0.76	2.86	2.00
Cold- and hot-water-soluble portions	2.58	2.52	3.50	2.60
Hemicelluloses	7.15	5.50	1.14	0
Cellulose	4.82	4.77	3.20	0
Lignin	39.95	34.15	34.76	32.26
Protein	32.70	36.26	50.22	60.61
Total accounted for	90.34	87.09	100.45	99.07

foregoing; the cellulose and hemicelluloses are either absent entirely or present only in low concentrations, while the nitrogen content is high. Although the relative protein concentration is greater than in the other soil types, it does not comprise most of the humus, as assumed by Remezov. Lignin is not lacking but is actually found in appreciable amounts. The higher protein content in this soil type is no justification for the assumption, which was not based upon experimental evidence, that the humus in serozems consists entirely of microbial cell substance. The possibility is not excluded that some of the nitrogen in these soils may be present, partly at least, in the form of other, non-protein compounds. The average C:N ratio of the two serozems analyzed here is 6.2, whereas the average C:N ratio for the Central Asiatic soils studied by Remezov was 4.5; this suggests the possibility that the humus

in the two American soils is not exactly the same as that of the Asiatic soils. The still narrower C:N ratio in the latter points to a considerable increase in protein content. The difference may here, as well, be due to a natural variation in soil types rather than to a marked change in the nature of the humus.

The rapid decomposition of the organic matter in serozem soils upon cultivation was brought out by Geltzer et al. (5), who found that in some cases as much as 53 per cent of the humus was destroyed upon cultivation for a period of 3 years. It is interesting to note that the loss of nitrogen was less than that of total humus, with the result that the C:N ratio became narrower, changing from 8.2:1 in the original soil to 6.2:1 in the cultivated soil. The humus content of the soil reached an equilibrium, the loss becoming smaller on continued cultivation; the equilibrium was at the lowest point when mineral fertilizers were used, indicating greater decomposition of the humus.

Attention has already been called to the fact that the findings of Geltzer, which are contrary to the results obtained by Remezov and those reported in this paper, of large quantities of hemicelluloses and cellulose in serozem soils were due to an insufficient consideration of the method of determination of these two groups of complexes in the humus. Geltzer determined the carbon in the portion of humus hydrolyzed by dilute mineral acid and calculated it as hemicellulose. This carbon is derived from carbohydrates only to a limited extent in the case of mineral soils; it is formed largely as a result of hydrolysis of some of the soil proteins and other compounds; it is also due partly to the destruction of some of the lignin on prolonged boiling with acid.

SUMMARY

Different soil types contain forms of humus which differ considerably in chemical composition.

Humus in podzols is characterized by a high cellulose, a high hemicellulose, and a low protein content. Because of a lack of bases in these soils, the two major constituents of the humus, namely, the lignin and protein, are readily dispersed in the water and are carried down to the lower horizons, where they are precipitated, in the presence of greater base concentration. One need not assume the existence of "humic acids" and "crenic acids," in order to explain the movement of specific organic complexes in the process of podzolization. This process can be much better understood when consideration is given to the mobility of the specific chemical constituents of humus under different soil and environmental conditions.

The humus of the tchernozems is characterized by a narrower carbon-nitrogen ratio, which is nearly 10:1, by a high content of lignin and protein, and by a lower cellulose and hemicellulose concentration. The humus in these soils is fixed because of the abundance of bases, namely, calcium and magnesium.

The humus in chestnut soils approaches in its chemical composition that of the tchernozems; it stands midway between these and the serozems. In

view of the fact, however, that only one soil belonging to this type was analyzed here, no broad conclusions can be drawn.

The humus of the serozems is characterized by a narrow carbon-nitrogen ratio of about 6:1. This is due to the relatively high protein content of this type of humus. Cellulose is completely absent. Hemicelluloses are either absent or present in very low concentrations. Lignins are present, but in somewhat lower amounts than in tchernozems.

As one proceeds from the podzols to the serozems, one finds the following gradual changes in the chemical composition of the humus: 1. A rapid disappearance of the cellulose and hemicelluloses, due to more active decomposition processes. 2. A rapid increase in the nitrogen content of the humus, because of the synthesizing activities of the microörganisms, accompanying the reduction of the carbohydrates. 3. The narrowing of the C:N ratio, based upon the preceding two phenomena. 4. A gradual reduction in lignin content, due to its greater decomposition.

Considerable variation was found among soils belonging to the same general type. Care must, therefore, be exercised in basing definite conclusions upon a large number of soils belonging to each soil type.

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THE AVAILABILITY OF SOIL POTASSIUM[1]

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The potassium content of most mineral soils is relatively high. This fact has led to the widespread belief that with proper methods of soil management the plant would be able to obtain all the potassium necessary for its best development. The method usually suggested involves an increase in the activity of the soil solvents by the use of organic matter in the form of green manure, crop residues, or farm manure.

Early results from the outlying soil experiment fields of Illinois, on gray soils low in general productivity, showed little need for potassium fertilization. After some 12 years of intensive legume cropping, accompanied by the liberal use of limestone considered necessary to grow the legumes, a marked response to potassium fertilization was observed. Twenty-five years' experimental results at the New York State College of Agriculture indicated that the addition of potassium to the soil increased crop yields, although the results for the first few years showed no increase. In these experiments it appears that the natural forces operating were not sufficient to provide adequate available potassium over a period of years, despite the fact that the soil was furnished with liberal amounts of lime and organic matter.

Many attempts have been made to correlate the water-soluble and exchangeable potassium of the soil with the availability of potassium to plants. Von Nostitz (28), Breazeale (7), and Magistad (24) believe that the plant's chief source of potassium is the water-soluble or exchangeable form. The last named investigator as well as Martin (25) also believes that the plant obtains part of its potassium from the non-replaceable form. Gedroiz (14), in his experiments, concluded that plants were able to obtain all the potassium necessary from the non-exchangeable form. Bartholomew and Janseen (3) found it possible to vary the amount of exchangeable potassium through a wide range by means of potassium fertilization. Schollenberger and Dreibelbis (30) and Crowther and Basu (12) found that exchangeable potassium was increased by potassium fertilization.

Some attention has been given the ratio of exchangeable calcium to exchangeable potassium. The assimilation of potassium is believed by von

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Nostitz (28) to be definitely related to the amount of lime and magnesia. The importance of this ratio has been mentioned by Barbier (2). Ehrenberg (13) pointed out the harmful influence to plant growth of increasing the supply of lime to a soil low in available potassium.

It has been suggested that the rate of solubility of soil potassium would offer an explanation of the difference between soils in their ability to provide the plant with this element. Bouyoucos (5) found soils differed in their rate of solubility, as measured by the depression of the freezing point, but concluded there was no close relation of this property to soil productivity. No determinations were made of individual solutes. Burd and Martin (9) found that the concentration of electrolytes in the displaced soil solution was higher in the spring than in the fall. This indicated to them that some soils may be unable to maintain during the whole season a concentration of nutrients sufficient to produce normal growth.

It is evident that the manner in which the soil provides the plant with available potassium is not well understood. The purpose of the following investigation is to contribute additional information to the subject.

METHODS OF ANALYSIS

Exchangeable potassium and calcium were extracted with normal ammonium acetate adjusted to a pH of 7.07 as suggested by Schollenberger and Dreibelbis (31). Such a solution has no significant secondary solubility effect, and a preliminary treatment with a strong alkali is unnecessary in order to replace all exchangeable hydrogen. One hundred cubic centimeters of the ammonium acetate solution was added to 10 gm. of air-dry soil in a 250-cc. Erlenmeyer flask, and the mixture was shaken for 10 minutes. The contents of the flask were transferred to a dry filter and washed twice with two 50-cc. portions of the ammonium acetate solution.

The determination of potassium in this extract was made by the sodium cobaltic nitrite method as used and described by Snider.[3] The solution of sodium cobaltinitrite was prepared by adding 25 gm. of the reagent to 100 cc. of water. The mixture was kept on ice one to two hours in the dark, filtered through asbestos, and held at 10°C. or below in the dark until needed. The solution obtained by extracting the soil with normal ammonium acetate was placed in 250-cc. beakers and evaporated to dryness on the steam bath. Five cubic centimeters of 5 to 10 per cent H_2O_2 was added to the residue, and the resulting solution was evaporated to dryness. The process was repeated three times. The residue was taken up with about 10 cc. of hot water, and 20 per cent NaOH was added until the solution was alkaline to phenolphthalein. The solution was boiled 3 to 10 minutes to expel traces of ammonia, the sides of the beaker were washed down with hot water during the process, and the boiling was continued until a volume of about 5 cc. was attained. The solu-

[3] The author is indebted to H. J. Snider of the Illinois Experiment Station for a description of the method followed.

tion was then filtered through a No. 00 9-cm. Swedish filter paper. The beaker and filter were washed with small amounts of hot water until the filtrate and washings, received in 250-cc. Pyrex beakers, reached a volume of about 25 cc. Beginning with the filtering process care was taken to exclude fumes of ammonia from the laboratory as was emphasized by Milne (26). The filtrate was made acid with 1–1 acetic acid, and then 5 drops more of the acid was added. Ten cubic centimeters of redistilled, 95 per cent, ethyl alcohol was added, and the beakers were placed on ice or otherwise reduced to a temperature of 10°C. or below. Five cubic centimeters of a 25 per cent solution of sodium cobaltic nitrite was then added, and the beakers were held at 10°C. or below in the dark for one to twenty-four hours. This solution, containing the precipitate of potassium cobaltinitrite, was filtered through the asbestos pad of a Gooch crucible which had just been washed with ice water. The precipitate was washed with 4-cc. portions of ice water until free of alcohol. Gentle suction was used. The crucible was placed pad intact into the original beaker, about 200 cc. of boiling water and 6 cc. of 6 *N* H_2SO_4 were added, and the mixture was titrated at once with about 0.05 *N* $KMnO_4$ to a faint permanent pink. The asbestos may be used repeatedly. One cubic centimeter of 0.05 *N* $KMnO_4$ is equivalent to 0.0003259 gm. of K.

The reagents used in the determinations were carefully prepared. The alcohol was redistilled. The asbestos was prepared according to the method described by Morrow (27) for sugar analysis. The potassium permanganate solution was stored in the dark and checked against sodium oxalate at frequent intervals. A blank determination of reagents was made for each series of determinations.

The cobaltic nitrite method has certain advantages over the ordinary platinic chloride procedure especially where small quantities of potassium are to be determined. However, since the method is open to criticism if not carefully controlled it was thought desirable to examine certain details of the procedure and to determine its reliability with the platinic chloride method.

A solution of K_2SO_4 was made up containing 0.5 mgm. of potassium per cubic centimeter. This concentration was checked by the platinic chloride method. Table 1 shows the influence of the time of standing after addition of the solution of cobaltinitrite to a solution containing 2 mgm. of potassium as K_2SO_4. The results indicate that a period of one hour is ample to precipitate the potassium from the solution.

Table 2 shows determination of potassium by the cobaltic nitrite method in a solution containing 0.5 mgm. per cubic centimeter.

In the case of 10-gm. soil samples 0.25 mgm. of potassium represents 25 p.p.m. It was found possible to check duplicate determinations of exchangeable potassium within 3 p.p.m. by means of the sodium cobaltic nitrite method.

The determination of total potassium in soils was made by fusing 1 gm. of soil with 5 gm. of Na_2CO_3; the flux was taken up with hot water and evaporated to dryness; and the silica was eliminated in the usual manner. The

filtrate from the precipitate of silica was made up to 250-cc. volume, and the potassium of a 25-cc. aliquot was determined by the cobaltic nitrite method.

To check the accuracy of this method the potassium was determined in the original samples of two New York soils, the total potassium of which had been

TABLE 1

Effects of time of standing on precipitation of potassium from K_2SO_4 solution to which has been added cobaltic nitrite solution

K_2SO_4 solution originally contained 2 mgm. K

TIME OF STANDING	K RECORDED	TIME OF STANDING	K RECORDED
hours	*mgm.*	*hours*	*mgm.*
¼	1.92	2	2.10
½	1.98	21	2.08
¾	1.94	51	2.23
1	2.02	78	2.02

TABLE 2

Potassium determination by cobaltic nitrite method

SOLUTION	K PRESENT	K FOUND	K RECOVERED
cc.	*mgm.*	*mgm.*	*per cent*
0.5	0.25	0.29	116
1.0	0.50	0.46	92
2.0	1.00	1.08	108
3.0	1.50	1.44	96
4.0	2.00	2.00	100
5.0	2.50	2.50	100
6.0	3.00	2.82	94
7.0	3.50	3.29	94

TABLE 3

Comparison of cobaltic nitrite and platinic methods of determining total potassium of New York soils

SOILS	POTASSIUM FOUND BY	
	Platinic chloride method	Cobaltic nitrite method
	per cent	*per cent*
21A	2.19	2.20
70A	1.56	1.54

determined by the platinic chloride method and reported by Bizzell (5). These soils were reported as 21A, a Volusia silt loam from Allegany County, and 70A, a Duchess silt loam from Duchess County.

Table 3 shows a comparison of cobaltic nitrite and platinic methods of determining the total potassium of two New York soils.

All determinations as reported were made in duplicate. In order to avoid any possibility of a systematic error the duplicate determinations in each case were made at different periods.

Exchangeable calcium was determined by precipitation as CaC_2O_4 and titration of the same with 0.1 *N* $KMnO_4$.

Nitrate nitrogen was determined colorimetrically in an extract obtained from one part of soil and five parts of water.

Base exchange capacity was determined by ammonia absorption. The soil was leached with ammonium acetate according to the method of Chapman and Kelley (10). The ammonium fixed by the soil was determined by digestion with an excess of MgO and distillation into 0.1 *N* H_2SO_4.

The hydrogen-ion concentration was determined by means of the quinhydrone electrode. Electrical resistance of solutions was determined by means of a modification of the wheatstone bridge, as designed by Briggs (8).

Relation of Crop Yields and Fertilization to Exchangeable Potassium

A history of the soils used is necessary before the results of the chemical studies are considered. The Ewing soil experiment field, located in southern Illinois, was established in 1910. The soil is a mature, imperfectly drained, gray silt loam, with a slowly pervious tight clay layer 18 to 20 inches below the surface. The slope is 3 per cent or less. The rotation was wheat (sweet clover seeding), corn, oats, and sweet clover seed crop, as described by Bauer, Smith, and Smith (4). The soil treatments were as follows:

R—residues, corn stalks, sweet clover catch crop. Straw was included previous to 1922
L—limestone, 9 tons applied during the period 1910–1922.
P—rock phosphate, 4 tons applied during the period 1910–1924.
K—Kainit, 400 pounds, applied before corn, and 400 pounds before wheat in the rotation.
M—barnyard manure. To the "M" alone plot 3.2 tons per the rotation ending 1930, and to the "ML" plot 8.9 tons per the same period, were applied before corn in each case. These amounts were equivalent to the dry weight of the crops removed from the respective plots.

After the use of limestone and sweet clover for about 12 years, the crops—especially corn—appeared to suffer from lack of potassium. The yields of corn for two periods are shown in table 4. This condition, although more serious at Ewing, was found under like circumstances on similar soils in other locations in the state.

In 1927 straw at the rate of 3 tons per acre was spread over the soil just after corn planting, left on the ground for 5 weeks, and then removed. Frequent rains occurred during the period. The yields for the RL and RLP plots indicate that available potassium was furnished by the straw. A decrease in available nitrogen, due to the increase in activity of the soil organisms, may also have been beneficial to the crop.

Soil samples representing the soil layers A_1, A_3, and B_1 were collected from the experiment field, June 1930.

The RL and RLP plots (table 5) show an average of 23 and 25 p.p.m. of exchangeable potassium in comparison with 31 p.p.m. for the untreated plot. Ames and Simon (1) as well as Crowther and Basu (12) obtained similar

TABLE 4

Ewing soil experiment field yields of corn with soil treatments indicated

SOIL TREATMENT	AVERAGE ACRE YIELD 1915–16	ACRE YIELD 1927	ADDITIONAL TREATMENT 1927	ACRE YIELD 1927
	bu.	*bu.*		*bu.*
O	21	2	Straw	7
R	17	1	Straw	7
RL	49	5	Straw	22
RLP	47	5	Straw	26
RLPK	60	52	Straw	50
ML	59	53	Straw	40

TABLE 5

Exchangeable potassium and pH of Ewing soil

SERIES	SOIL LAYERS	SOIL TREATMENT AND PLOT NUMBER													
		2 M		3 ML		6 R		7 RL		8 RLP		9 RLPK		None	
		K	pH	K	pH	K	pH	K	pH	K	pH	K	pH	K	pH
		p.p.m.		*p.p.m.*		*p.p.m.*		*p.p.m.*		*p.p.m.*		*p.p.m.*		*p.p.m.*	
100	A_1	41	4.7	38	7.6	31	4.3	23	7.7	14	7.7	58	7.7	23	4.6
100	A_3									21	5.1	28	5.3	28	4.7
100	B_1									115	5.2	132	5.2	122	5.4
200	A_1	38	4.8	28	6.8	35	4.8	20	7.2	31	7.3	40	6.8	28	4.9
200	A_3									25	5.0	33	5.2	33	4.9
200	B_1									126	5.0	142	4.7	144	5.1
300	A_1	39	4.4	50	6.7	40	4.4	23	6.5	27	6.8	40	6.6	39	4.6
300	A_3									28	5.2	30	5.0	88	4.8
300	B_1									104	5.2	104	5.0	165	5.3
400	A_1	50	4.5	52	6.7	47	4.5	26	6.4	30	6.2	92	6.3	36	4.5
400	A_3									48	5.4	47	5.5	47	4.9
400	B_1									125	4.8	136	5.0	119	5.1
Av.	A_1	42		42		38		23		25		56		31	
Av.	A_3									30		34		49	
Av.	B_1									117		128		137	

results. The experiments of Bartholomew and Janseen (3) indicated that plants could reduce the exchangeable potassium below 25 p.p.m. only with difficulty.

Potassium fertilization doubled the exchangeable potassium, as shown in

table 6, but this rapidly falls to the lower level apparently as a result of removal by crops. The manure (table 7) maintains a level little higher than that of the untreated plots, but furnished a supply adequate for large crop yields.

TABLE 6

Effect of kainit on the exchangeable potassium of the Ewing soil

Soil samples collected June 1930

400 LBS. KAINIT APPLIED FOR		PLOT	K FOUND
Crop of	Crop of		
			p.p.m.
1927	1930	109	58
1927	1928	209	40
1928	1929	309	40
1929	1930	409	92

TABLE 7

Effect of manure on the exchangeable potassium of the Ewing soil

Soil samples collected June 1930

CROP OF	3.2 TONS MANURE PER ACRE		8.9 TONS MANURE PER ACRE	
	Plot	K found	Plot	K found
		p.p.m.		*p.p.m.*
1927	102	41	103	38
1928	202	38	203	28
1929	302	39	303	50
1930	402	50	304	52

TABLE 8

Total and exchangeable potassium, Ewing soil

Expressed in pounds per acre

PLOT	SOIL LAYER	EXCHANGEABLE K	TOTAL K
108	A_1	14	12,500
	A_3	21	13,700
	B_1	115	14,300
109	A_1	58	12,500
	A_3	28	13,400
	B_1	132	13,700

The high amount of exchangeable potassium of the B_1 soil layer (table 8) compared with that of the upper layers, suggests that potassium carried in solution from the surface soil was fixed to some extent in the B_1 by replacing other cations of the soil complex. Or that the replaceable potassium of this

layer was not changed through leaching or soil management to the extent of that of the surface layer. The former theory has been suggested by Lyon, Bizzell, Wilson, and Leland (21), and by MacIntire (22). It would seem probable that this region of higher concentration would offer a supply of readily available potassium to deep-rooted legumes. The growth of sweet clover and succeeding crops, on plots receiving no potassium fertilization, on the Ewing field does not agree with this theory.

THE RELATION OF TOTAL TO EXCHANGEABLE POTASSIUM

There is little relation between the total potassium and the exchangeable potassium; plot 109 A_1 layer (table 8) has over four times as much of the latter form as the same layer plot 108, yet both have the same amount of total potassium. The B_1 layer plot 108 has less exchangeable potassium, and more of the total, than the same layer plot 109.

RELATION OF EXCHANGEABLE CALCIUM TO EXCHANGEABLE POTASSIUM

The relations of exchangeable calcium to exchangeable potassium are brought out in table 9. Fertilization increased the exchangeable calcium in the surface layer and in the A_3 layer, but it affected the potassium of the surface layer only.

In many instances the heavy application of limestone lowered the hydrogen-ion concentration below the neutral point and retarded the rate of change from the complex to simple forms of soil potassium. The work of Lyon, Bizzell, Wilson, and Leland (21), Magestad (24), MacIntire (22), and others bears out this idea. It was found by analysis that the limed soils of the Ewing field contained no calcium as calcium carbonate. Tables 9 and 10 reveal that the adsorptive complexes of the limed soils were practically saturated with calcium in the A_1 layer. MacIntire and Sanders (23) suggested that such freshly formed calcium and magnesium absorption complexes were more readily hydrolyzable than freshly formed potassium absorption complexes.

The ratio of calcium to potassium in the untreated soil was 28; in the RLPK plot, 59; and in the RLP plot, 180. Such a wide ratio as the last might lead to serious nutritional disturbances of the plant. Von Nostitz (28) believes that a certain ratio of calcium to potassium is best for normal growth. Ehrenberg (13), Lagatu and Maume (18), and Lipman, Blair, and Prince (19) have pointed directly to a decreased absorption of potassium by plants due to liming. Volk and Truog (34) believe that calcium antagonism to potash absorption may explain some of the pronounced responses to potash fertilization obtained on neutral and calcareous soils high in nitrates and hence in soluble calcium salts.

A relatively high concentration of calcium in the soil solution may retard the entrance of potassium into the plant. True (33) believes that the presence of a certain amount of available calcium in the cultural solution is necessary to maintain normal permeability relations of the cells of absorbing roots of

TABLE 9

Effect of cropping and fertilization on exchangeable potassium and calcium

Milligram equivalents of exchangeable calcium and potassium, the base exchange capacity, and the pH of Ewing soil.

PLOT	SOIL LAYER	TREATMENT	CALCIUM	POTASSIUM	AMMONIA ABSORBED	pH
			m.e.	*m.e.*	*m.e.*	
108	A_1	RLP	9.2	0.036	9.0	7.7
	A_3	RLP	3.6	0.054	8.5	5.1
	B_1	RLP	3.4	0.294	19.5	5.2
109	A_3	RLPK	9.0	0.148	9.7	7.7
	A_3	RLPK	4.2	0.072	8.7	5.3
	B_1	RLPK	4.5	0.341	21.0	5.2
110	A_1	O	1.4	0.059	8.2	4.6
	A_3	O	1.5	0.072	9.0	4.7
	B_1	O	3.9	0.313	20.5	5.4
208	A_1	RLP	8.8	0.079	8.5	7.3
	A_3	RLP	3.5	0.064	6.4	5.0
	B_1	RLP	3.6	0.323	20.0	5.0
209	A_1	RLPK	7.7	0.104	9.0	6.8
	A_3	RLPK	3.7	0.084	7.5	5.2
	B_1	RLPK	4.3	0.363	20.0	4.7
210	A_1	O	1.8	0.072	7.9	4.9
	A_3	O	2.5	0.084	9.2	4.9
	B_1	O	4.4	0.369	23.4	5.1
308	A_1	RLP	9.1	0.069	8.6	6.8
	A_3	RLP	3.7	0.072	7.8	5.2
	B_1	RLP	3.4	0.266	13.3	5.2
309	A_1	RLPK	7.8	0.104	9.5	6.6
	A_3	RLPK	3.6	0.077	8.1	5.0
	B_1	RLPK	4.3	0.266	17.0	5.0
310	A_1	O	3.0	0.100	9.1	4.6
	A_3	O	2.4	0.215	10.5	4.8
	B_1	O	5.6	0.422	22.5	5.3
408	A_1	RLP	9.0	0.074	10.6	6.2
	A_3	RLP	6.2	0.126	10.1	5.4
	B_1	RLP	5.0	0.320	18.9	4.8
409	A_1	RLPK	8.8	0.236	10.5	6.3
	A_3	RLPK	5.5	0.120	9.9	5.5
	B_1	RLPK	5.6	0.348	20.3	5.0
410	A_1	O	3.2	0.092	9.9	4.5
	A_3	O	3.1	0.120	10.2	4.9
	B_1	O	4.1	0.300	18.9	5.1

TABLE 10

The ratio of milligram equivalents of exchangeable calcium to exchangeable potassium, of calcium to base exchange capacity, and of potassium to Ewing soil

PLOT	SOIL LAYER	TREATMENT	RATIO CALCIUM TO POT	RATIO CALCIUM TO ABSORBED AMMONIA	RATIO POTASSIUM TO ABSORBED AMMONIA
108	A_1	RLP	256	1.02	0.004
	A_3	RLP	67	0.24	0.006
	B_1	RLP	11	0.18	0.015
109	A_1	RLPK	61	0.93	0.015
	A_3	RLPK	60	0.48	0.008
	B_1	RLPK	13	0.21	0.016
110	A_1	O	24	0.17	0.007
	A_3	O	21	0.17	0.008
	B_1	O	13	0.19	0.015
208	A_1	RLP	111	1.04	0.009
	A_3	RLP	55	0.55	0.010
	B_1	RLP	11	0.18	0.016
209	A_1	RLPK	74	0.86	0.010
	A_3	RLPK	44	0.49	0.011
	B_1	RLPK	12	0.22	0.018
210	A_1	O	25	0.20	0.009
	A_3	O	30	0.27	0.009
	B_1	O	12	0.19	0.016
308	A_1	RLP	232	1.06	0.008
	A_3	RLP	51	0.47	0.009
	B_1	RLP	13	0.26	0.020
309	A_1	RLPK	75	0.82	0.011
	A_3	RLPK	47	0.44	0.010
	B_1	RLPK	16	0.25	0.016
310	A_1	O	30	0.33	0.010
	A_3	O	11	0.23	0.022
	B_1	O	13	0.25	0.042
408	A_1	RLP	122	0.85	0.007
	A_3	RLP	24	0.62	0.013
	B_1	RLP	16	0.27	0.017
409	A_1	RLPK	37	0.84	0.023
	A_3	RLPK	46	0.55	0.012
	B_1	RLPK	16	0.28	0.017
410	A_1	O	35	0.32	0.009
	A_3	O	26	0.30	0.012
	B_1	O	14	0.22	0.016

higher green plants. Eckerson working with True (33), using young corn plants, substituted the calcium of the culture solution with potassium. An increase in permeability occurred, and the content of the root cells moved outward with fatal results to the plants. It is reasonable to believe that this reaction would be reversible to some extent, and in a solution containing an excess of calcium the effect on permeability may be such as to retard the entrance of essential ions.

The poor growth of corn on the Ewing field occurred on those plots where the conditions favored a high concentration of calcium in the soil solution: a soil high in nitrates with an adsorptive complex saturated with calcium. Whiting and Richmond (35) working with soils similar to that of the Ewing field found that plowing in a crop of sweet clover for corn often supplied 150 pounds of nitrogen per acre. This would be equivalent to over 650 pounds of nitric acid in its action on the soil bases. Sears (32) found a reduction of nitrate content as well as an addition of potassium salts beneficial on certain alkali soils of northern Illinois.

In cases where lime causes a decrease in growth the effect may be due to the decrease in permeability caused by the calcium with a consequent decrease in intake of the essential elements. The addition of any cation which would increase permeability should prevent the injurious effect of calcium. Kainit, a mixed salt, has been very effective in relieving potassium deficiency on the Ewing field, possibly for this reason. Gerlach (15) and many others have presented evidence to show that sodium partially replaces potassium where the latter is present in small amounts.

RATE OF SOLUBILITY OF SOIL POTASSIUM

It has been suggested that the rate of solubility of soil potassium is a better index of availability than is the amount soluble at a given time. The Ewing soil already described and four New York State soils were selected for study. The New York soils were as follows: an Ontario loam from Monroe County and a Volusia silt loam from Turkey Hill, Tompkins County. The first two of these soils responded to potassium fertilization; the last two did not, as reported by Lyon (20).

The soils were leached with distilled water until the electrical resistance of the leachate approached the resistance of distilled water. At this point it was assumed that the materials capable of carrying an electric current, which would include the highly ionized potassium compounds, had been carried out of the soil. The soils were air dried and held at room temperature and optimum moisture for 30 days and again leached. Following this it was again air dried and held under the same conditions for 180 days and leached a third time.

The first and second leachings were collected in successive portions representing 100 cc. of leachate per 50 gm. of soil. The potassium was determined in each portion. The third leaching process was so slow as a result of the

puddled condition of the soil that no attempt was made to divide it into separate portions. The results are shown in table 11.

All the soils were rapidly reduced to the point where about the same amount of potassium was found in successive portions of the leachate. There seemed to be little substantial increase in this amount during the period of incubation. Barbier (4) found that in extracting a soil by percolation with water the first portions of the percolate contained practically all the water-soluble potassium.

TABLE 11

Potassium extracted by successive portions of distilled water, 100 cc. per 50 gm. of soil, and electrical resistance of extract

100-cc. PORTIONS DISTILLED WATER	ONTARIO		DUTCHESS		VOLUSIA ALLEGHENY		VOLUSIA TURKEY HILL	
	K	Resistance	K	Resistance	K	Resistance	K	Resistance
	p.p.m.	*ohms*	*p.p.m.*	*ohms*	*p.p.m.*	*ohms*	*p.p.m.*	*ohms*
1	4.1	550	14.0	250	15.0	700	28.5	1150
2	3.8	5000	3.2	1600	8.8	2900	12.4	2700
3	3.0	7250	1.6	5000	6.1	5500	8.6	5000
4	3.7	8000	2.9	6500	7.9	8000	13.5	6500
5		9000		8500		9000		8750
6	...	....		9000		....		9000
Total....	14.6		22.7		37.8		63.0	
Soil incubated 30 days at room temperature and optimum moisture								
1	2.7	3000	2.6	4300	3.1	3300	2.8	4200
2	2.1	5500	2.0	8500	4.2	7000	2.8	6800
3	2.4	6000	1.2	9000	3.4	9000	2.6	9000
4	2.7	9000	2.0	9000	2.8	9000	2.3	9000
5	...	....	2.3	9000	3.1	9000	2.3	9000
Total....	9.9		10.1		16.6		12.6	
Soil incubated 180 days at room temperature and optimum moisture								
1	...	1500	...	1000	...	2300	...	1200
2	...	2900	...	2800	...	4500	...	2600
3	...	3000		5000	...	5500	...	6000
Total....	3.3		4.1		6.2		5.3	

Exchangeable potassium was determined before and after each leaching. The results indicate (table 12) that a part of that recovered in the leachate had been at the expense of the replaceable form. Coles and Morison (11) by alternate washing and drying at 98°C. were able to remove all the exchangeable bases from soils.

The Turkey Hill Volusia, which showed the largest increase for potassium fertilization (20), gave the highest amount of water-soluble potassium. On-

tario loam gave no increase for such fertilization and contained a small amount of water-soluble and exchangeable potassium.

Water-soluble potassium does not represent the entire amount in the soil available to plants, but if the soil were able to maintain the concentrations found, according to Parker and Pierre (29) it would be ample for plant needs. Hoagland and Martin (17) found that the concentration of potassium present in the displaced soil solution before and after growth of a crop could be very low yet effect an adequate supplying power.

TABLE 12

Potassium leached from soils with distilled water at the intervals and with the soil treatment indicated, and NO_3 at the time of leaching

SOIL	NO. 3	K FIRST LEACHING	SOIL TREATMENT*	NO. 3	K LEACHED AT 30 DAYS	SOIL TREATMENT	NO. 3	K LEACHED AT 210 DAYS
	p.p.m.	*p.p.m.*		*p.p.m.*	*p.p.m.*		*p.p.m.*	*p.p.m.*
Ontario	230	10.9	None	28	6.2	None	130	3.3
			Sugar N	40	3.9	Sugar NLP	86	4.1
Dutchess	612	18.8	None	49	5.8	None	175	4.1
			Sugar N	33	6.1	Sugar NLP	26	3.9
Volusia A_1	160	29.9	None	43	10.7	None	49	6.2
			Sugar N	37	6.0	Sugar NLP	432	3.5
Volusia Turkey Hill	23	49.5	None	40	8.2	None	216	5.3
			Sugar N	47	5.1	Sugar NLP	286	2.3
Ewing 110				58	5.7	None	135	3.3
						Sugar NLP	203	1.2
Ewing 110L					2.7	None	154	2.0
Ewing 107				34	4.1	None	115	5.0
						Sugar NLP	124	4.5

* Soils were maintained at room temperature and optimum moisture during the interval between leachings. After the first leaching, 3,000 p.p.m. dextrose and $(NH_4)CO_3HO$ equivalent to 150 p.p.m. of NO_4 were applied. After the second leaching, in the case of the New York soils, and after the first, in the case of Ewing soil, dextrose at the rate of 5,000 p.p.m., $(NH_4)_2CO_3 \cdot H_2O$ equivalent to 200 p.p.m. of NO_4, 56 p.p.m. of superphosphate, and 2,000 p.p.m. of lime as finely ground $CaCO_3$ were applied.

After the first leaching, 3,000 p.p.m. dextrin and $(NH_4)_2CO_3 \cdot H_2O$ equivalent to 130 p.p.m. of nitrate were added to a part of each soil. After the second leaching, to the same soils were applied dextrin at the rate of 5,000 p.p.m., $(NH_4)_2CO_3 \cdot H_2O$ equivalent to 200 p.p.m. of nitrate, 56 p.p.m. of superphosphate, and 2,000 p.p.m. of finely ground limestone. The appearance of nitrate nitrogen was considered an indication that the soil organism had used up the sugar.

We may represent the process of the change from the complex to the simple form of soil potassium, by the following reaction:

$$2KA + H_2CO_3 \rightleftharpoons 2HA + K_2CO_3$$

in which KA represents the complex form. Factors forcing the reaction to the right are the pressure of CO_2 and removal of the product K_2CO_3. Theoretically, high activity of the soil organisms should bring about both these conditions. A reduction in their activity would force the reaction toward

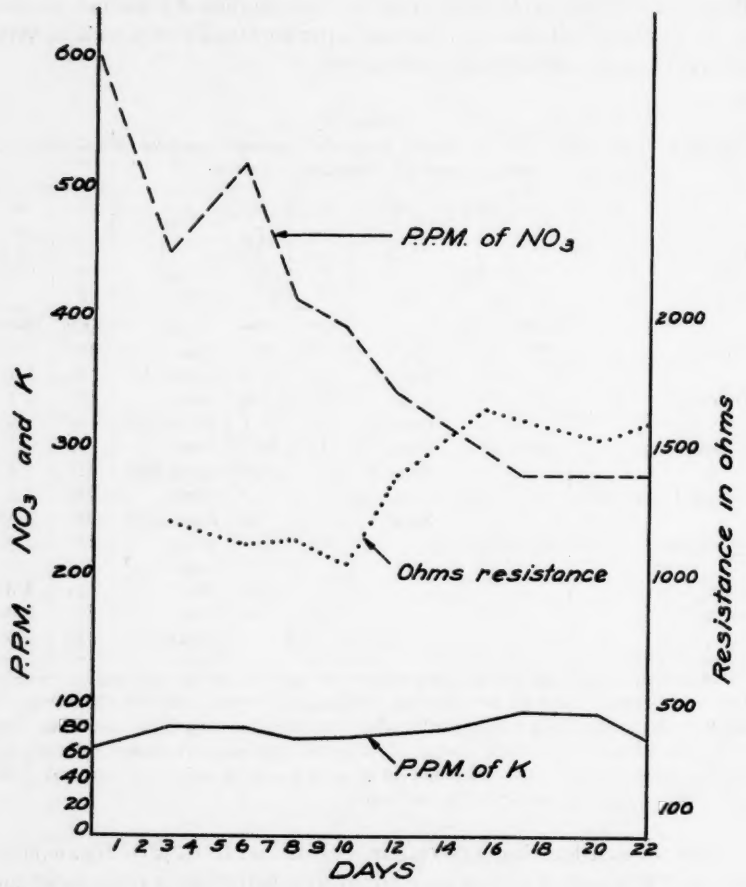

FIG. 1. EFFECT OF THE ADDITION OF 5,000 P.P.M. OF DEXTRIN TO A DUTCHESS SILT LOAM ON THE POTASSIUM EXTRACTED BY $NH_4C_2H_3O_2$, ON THE NO_3 CONTENT, AND ON THE RESISTANCE OFFERED TO AN ELECTRIC CURRENT BY A 5.1 WATER EXTRACT

the left, as a result of a decrease in CO_2 pressure and the increased amount of the simple form of potassium. Bartholomew and Janseen (5) contend that such a reaction is readily reversible.

The results (table 12) show that at the end of the first incubation period

only one soil receiving dextrose and ammonium carbonate had more water-soluble potassium than the untreated soil. With some of the soils it was thought possible that the activity of the soil organism was still at a relatively high level, and a part of the easily soluble potassium might have been held in their bodies.

The following experiment was carried out in order to determine the influence of an increase in number of the soil organisms upon the exchangeable potassium. Dextrin at the rate of 5,000 p.p.m. was added to a Duchess silt loam, and at frequent intervals determinations were made of total nitrates, exchangeable potassium, and water-soluble materials by the resistance method. The results are shown in figure 1.

The nitrates and total electrolytes showed a steady decrease in concentration; but, after 16 days remained constant. Exchangeable potassium shows a slight increase. It is possible that the demands of the increased numbers of soil organisms were balanced by the solubility effect of the increased CO_2 pressure. Hibbard (16) found that the liberation of much CO_2 is not necessarily followed by a great increase of solubility of soil minerals.

SUMMARY

On the Ewing soil high crop yields were maintained only by the addition of potassium.

Potassium fertilization increased the amount of exchangeable potassium until utilized by the crop.

The B_1 soil layer contained much more adsorbed potassium than the A_1 or A_3.

No relation was found between the total and exchangeable forms of soil potassium.

Fertilization did not affect the exchangeable potassium of the A_3 or B_1 layer or the exchangeable calcium of the B_1 layer.

Potassium starvation in the Ewing soil was associated with low exchangeable potassium and high exchangeable calcium.

The methods used showed no significant difference in the rate at which exchangeable and water-soluble potassium were replenished from the reserve supply of the soils.

There appears to be little relation between response to potassium fertilization and exchangeable or water-soluble potassium for the soils used.

The addition of sugar to a soil high in nitrates reduced the nitrate level, reduced the level of electrolytes, and slightly increased the exchangeable potassium.

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A SIMPLE METHOD OF ESTIMATING EXCHANGEABLE CALCIUM AND OTHER BASES IN NON-CALCAREOUS SOILS

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The determination of exchangeable Ca in non-calcareous soils is very important because if this exchangeable base falls below a certain value Ca deficiency will result, necessitating liming. Apparently such estimations present no serious difficulties in the sense that, on account of the absence of $CaCO_3$, there are no complications introduced through solubility effects. Simplification of the technique, however, appeared feasible, and the present investigation was undertaken with that object in view.

Since Ca is precipitated quantitatively as Ca oxalate, it seemed reasonable to expect that if standard oxalic acid be added to soil in the presence of a reagent that would bring the exchangeable Ca into solution, the decrease in the concentration of oxalate ion would be equivalent to the amount of exchangeable Ca in the soil. A number of experiments were performed to study the conditions under which the complete precipitation of Ca takes place. These are discussed in this paper.

EXPERIMENT

In order to standardize the working details, several preliminary experiments were carried out in which a heavy black cotton soil, possessing a high base exchange capacity, was used. The soil was first treated with 0.05 *N* HCl, to free it from carbonates and exchangeable bases, then leached with water. The soil still retained 8.8 m.e. of Ca per 100 gm. To 5-gm. portions of this soil increasing amounts of $Ca(OH)_2$ solution were added and left overnight. Next morning, standard oxalic acid solution was added to the suspension, and the total volume of the solution (without the soil) was made up to 150 cc. in every case. In one series, approximately 1 gm. of solid potassium acetate was added to each suspension; the second series was left as it was. The suspensions were left for 4 hours with occasional shaking and then filtered through a fluted filter. Seventy-five cubic centimeters of the filtrate was taken and titrated against standard $KMnO_4$ solution. The decrease in the concentration of oxalate ion was reckoned equivalent to the total exchangeable Ca. The results given in table 1 show that the whole of the Ca is accounted for in the K acetate series, but a considerable amount was left in the soil when this reagent was not added.

In the next experiment, the precipitation of Ca oxalate was tried in the presence of 0.5 *N* acetic acid. The results given in table 2 show that the presence of acetic acid has practically no effect on the precipitation of exchangeable Ca by oxalic acid alone. If anything, the amount of Ca left in the soil is slightly more with acetic acid than without it.

TABLE 1

Precipitation of exchangeable Ca as oxalate with and without K acetate

All values in milliequivalents per 5 gm. of soil

Ca PRESENT	Ca FOUND WITHOUT K ACETATE	WITH K ACETATE
1.405	0.40	1.68
2.370	1.40	2.50
3.335	2.37	3.32
4.200	3.04	4.19
5.265	4.00	5.10

TABLE 2

Precipitation of exchangeable Ca with oxalic acid in the presence of 0.5 N *acetic acid*

All values in milliequivalents per 5 gm. of soil

Ca PRESENT	Ca FOUND
1.44	0.12
2.44	1.33
3.44	2.00
4.44	3.26
5.54	4.10

TABLE 3

Precipitation of exchangeable Ca with oxalic acid in the presence of increasing amounts of acetic acid, with and without K acetate

SOIL	STRENGTH OF ACETIC ACID	Ca PRESENT	Ca FOUND	
			With K acetate	Without K acetate
gm.	*N*	*m.e.*	*m.e.*	*m.e.*
0	0	3.82	....	3.82
0	0	3.82	....	3.78
5	0	4.26	4.18	3.13
5	0.05	4.26	3.82	2.91
5	0.01	4.26	3.98	3.10
5	0.2	4.26	3.63	2.97
5	0.5	4.26	3.45	2.86

Increasing concentrations of acetic acid were next tried both with and without K acetate. The results given in table 3 show that the greater the concentration of acetic acid, the smaller is the amount of exchangeable Ca precipitated. In the absence of the soil, however, the whole of the Ca is precipitated by oxalic acid, with or without acetic acid.

The failure of acetic acid to bring about the complete replacement of Ca in the soil is very interesting and most probably is due to the fact that Ca-oxalate cannot be precipitated completely unless the pH value of the solution is above 3.5. Since the soil with acetic acid and oxalic acid constitutes a system with a pH value less than 3.5, a part of the Ca oxalate dissolves and is again taken up by the soil with the liberation of oxalic acid, with the result that a part of the exchangeable Ca remains in the soil. In this connection a novel experiment was performed illustrating chemical reaction between two insoluble substances: 5 gm. of the acid treated soil was shaken for an hour with some Ca

TABLE 4

Decomposition of calcium oxalate by soil containing increasing amounts of calcium

0.1 *N* $Ca(OH)_2$ added to 5 gm. of soil	pH value	0.1 *N* oxalic acid brought into solution	
		With acetic acid	Without acetic acid
cc.		*cc.*	*cc.*
0	4.52	10.7	8.1
7.84	5.28	9.6	3.1
15.68	6.28	5.2	0.5
23.52	8.58	4.4	0.3
31.36	9.53	3.6	0.5
39.20	10.20	2.9	0.4

TABLE 5

Precipitation of exchangeable Ca in the presence of increasing amounts of KOH

The soil contained 4.36 m.e. of exchangeable Ca

0.1 *N* KOH solution	Calcium precipitated
cc.	*m.e.*
0	3.05
10	3.35
20	3.58
30	3.84
40	4.20
50	4.32

oxalate suspended in 100 cc. of water. When the suspension was filtered, it was found to contain 8.1 cc. of 0.1 *N* oxalic acid, showing thereby that apparently insoluble soil colloids are capable of decomposing insoluble Ca oxalate, a feat characteristic of the so-called strong acids only. In the light of this experiment it is not difficult to understand the decomposition of insoluble calcium phosphate by an acid soil.

The decomposition of Ca oxalate was next tried with the same soil after the addition of increasing amounts of $Ca(OH)_2$, both with and without acetic acid. The results given in table 4 show that in the presence of 0.5 *N* acetic acid, the soil is able to decompose calcium oxalate even when it is saturated with cal-

cium, pH 10. On the other hand in the absence of acetic acid the soil practically ceased to react with calcium oxalate when it contained enough Ca to give a pH value of 6.28.

Since the decomposition of calcium oxalate by the soil is mainly due to the low pH value of the reaction medium, this may not take place if the pH value of the soil be raised by the addition of alkali. This is illustrated in table 5, which records the results of an experiment in which 5-gm. portions of the acid treated soil were left with standard $Ca(OH)_2$ solution overnight. Next morning 10 cc. of *N* oxalic acid and increasing amounts of 0.1 *N* KOH were added and the total volume (without the soil) was made up to 150 cc. The suspension was shaken for an hour and filtered. Seventy-five cubic centimeters of the filtrate was titrated with permanganate as usual. It will be seen from table 5 that when the oxalic acid was half neutralized the whole of the exchangeable Ca was precipitated.

TABLE 6

Precipitation of exchangeable Ca in the presence of increasing concentrations of potassium acetate

The soil contained 4.4 m.e. of Ca per 5 gm.

SHAKING TIME	Ca FOUND K ACETATE IN 150 CC.								
	0 gm.	0.1 gm.	0.2 gm.	0.3 gm.	0.5 gm.	0.75 gm.	1.0 gm.	1.5 gm.	2.0 gm.
hours	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*
1	2.98	3.28	3.30	3.40	4.06	4.32	4.38	4.36	4.39
2	3.04	3.04	3.22	3.44	3.98	4.28	4.37	4.37	4.47
3	3.06	3.06	3.24	3.44	3.85	4.34	4.45	4.35	4.41

In order to find the minimum quantity of potassium acetate required to bring about the complete precipitation of replaceable Ca by oxalic acid, 5-gm. portions of the soil containing 4.4 m.e. of Ca were shaken for varying lengths of time with oxalic acid in increasing strengths of potassium acetate, and Ca was determined as usual by the decrease in the concentration of oxalic acid. The results, given in table 6, show that the whole of the exchangeable Ca is precipitated as oxalate in 1 per cent solution (approximately 0.1 *N*) of potassium acetate by shaking for 1 hour.

The possibility of Mg being precipitated along with Ca was explored by precipitating Ca in the presence of increasing amounts of magnesium acetate solution. The results given in table 7 show that Mg is not precipitated under these conditions; hence, exchangeable Ca could be determined in soils containing fairly large amounts of exchangeable Mg.

DETAILED DESCRIPTION OF THE PROPOSED METHOD

Soil in 10 to 20-gm. lots is shaken for 1 hour with 100 cc. of 0.1 *N* oxalic acid in 0.2 *N* potassium or ammonium acetate. This solution can be prepared as a stock solution. After being shaken, the suspension is filtered through a

fluted filter paper, and 50 cc. of the filtrate is titrated with standard permanganate after the addition of H_2SO_4 in the usual way. The total decrease in the concentration of the oxalate ion is equivalent to the exchangeable calcium in the soil.

Humus soils when treated with ammonium acetate and oxalic acid give a colored filtrate which cannot be titrated directly with permanganate. For such soils the method is modified as follows: 50 cc. of the filtrate is treated with 50 cc. of 0.1 *N* $CaCl_2$ solution, which precipitates the remaining oxalic acid. The precipitate of Ca oxalate is filtered, washed, and ignited until all the Ca oxalate is converted into CaO. This CaO is mixed with a certain amount of impurities, such as the oxides of Fe and Al, derived from the soil and cannot be weighed directly. To the residue after ignition, therefore, is added a known amount of standard acid, which is back titrated with alkali.

The decrease in the concentration of the acid is equivalent to the CaO neutralized, which is equivalent to the oxalic acid remaining in the solution. This quantity when substracted from the amount originally present in the solution, gives the decrease in the concentration of oxalic acid, which is equivalent to the exchangeable Ca in the soil. The results obtained by titrating the ignited

TABLE 7

Precipitation of Ca in the presence of increasing amounts of Mg

Total volume—150 cc.

Mg present, *gm.*	0	0.258	0.518	0.776	1.035	1.293	1.554	2.070
Ca found, *m.e.*	3.88	4.00	3.98	3.90	3.94	3.90	3.90	3.95

residue with standard acid are practically the same as those obtained by dissolving it in acid, reprecipitating Ca as oxalate, and estimating it by titration with permanganate in the usual way.

In order to compare the method outlined in this paper with other standard methods of determining exchangeable Ca, ten soils were examined, the normal ammonium acetate and ammonium chloride leaching being used for comparison. In every case 10 gm. of the soil was leached with 1 liter of the solution. The results given in table 8 show good agreement except in the case of soil 3, the significance of which will be brought out later.

The difficulty of replacing all the calcium in a soil by simple leaching with a neutral salt or an acid is not generally recognized. This will be clear from table 9, in which are recorded the results of an experiment in which 10-gm. portions of a soil containing 66 m.e. of Ca per 100 gm. of soil were leached with different solutions in 100-cc. lots. Calcium was estimated in successive 500 cc. of the leachates. It will be seen that in almost every case even the fifth lot contains some Ca and the total amount obtained even by such prolonged leaching in several cases falls short of the value obtained by the proposed method. Table 9 also indicates the comparative efficiency of the various rea-

gents in bringing about the replacement of Ca. It will be seen that 0.5 *N* acetic acid is probably the least effective. The use of this reagent for estimating exchangeable bases in soils, as suggested by Williams,[1] cannot, therefore, be recommended in the light of these experiments. Exchange reactions being mainly ionic, the slowness of acetic acid is obviously due to its low ionization constant.

TABLE 8

Exchangeable Ca in soils determined by different methods

SOIL NUMBER	pH	CLAY	EXCHANGEABLE Ca PER 100 GM.		
			Ammonium Acetate	Ammonium Chloride	Proposed method
		per cent	*m.e.*	*m.e.*	*m.e.*
3	7.64	63.8	53.8	53.1	59.6
6	5.29	31.6	5.1	4.9	5.4
9	5.76	22.8	3.8	4.45	4.6
12	5.84	14.8	3.6	3.95	3.2
14	5.37	31.5	2.8	3.75	5.0
15	7.71	27.6	13.0	13.90	12.0
18	5.79	25.1	4.0	4.30	3.6
20	5.64	15.1	3.1	1.80	2.2
22	6.85	17.8	7.85	8.10	8.5
23	7.41	11.8	8.20	9.05	9.0

TABLE 9

Replacement of Ca by leaching with different reagents compared with the proposed method

METHOD	Ca IN SUCCESSIVE 500-CC. LEACHATES					
	1	2	3	4	5	Total
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*
N ammonium acetate	59.75	1.8	0.3	0.65	0.15	62.65
0.2 *N* ammonium acetate	55.65	3.4	1.2	0.6	....	60.85
N ammonium chloride	61.6	2.35	1.6	0.2	1.3	66.05
N NaCl	59.9	2.5	1.55	0.8	0.5	65.25
0.2 *N* NaCl	44.95	7.4	3.85	2.25	....	58.45
N KCl	59.3	2.4	1.3	1.1	1.15	65.25
0.2 *N* KCl	54.0	4.65	1.5	0.65	0.8	61.6
0.05 *N* HCl	57.95	0.5	0.9	0.8	0.1	60.25
0.5 *N* Acetic acid	43.75	8.35	4.3	3.0	2.1	61.5
Proposed method	.....	....	....	....	....	66.3

The difficulty of replacing exchangeable Ca is so much greater in the case of humus soils that it is practically impossible to replace the whole of the Ca with a reasonable amount of leaching. This will be clear from table 10, which

[1] Williams, Rice, 1928. The determination of exchangeable calcium in carbonate free soils. *Jour. Agr. Sci.* 18: 439.

records the exchangeable Ca in a number of humus soils by the proposed method and by leaching with *N* ammonium acetate in 100-cc. lots, Ca being determined in 500-cc. lots. As in every case a colored filtrate was obtained, the modified technique was used and Ca was determined both by titrating the CaO in the ignited residue (A) and by dissolving the residue in acid and reprecipitating Ca as oxalate, followed by filtration and titration with permanganate (B).

TABLE 10

Exchangeable Ca in humus soils by the proposed method compared with N Ammonium acetate leaching

SOIL NUMBER	LOSS ON IGNITION	EXCHANGEABLE Ca PER 100 GM.						
		In successive 500-cc. leachates					Proposed method	
		1	2	3	4	Total	A	B
	per cent	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*
404	35.9	54.2	8.75	2.35	1.50	66.8	66.5	67.6
405	9.4	17.8	2.5	0.6	0.25	21.15	28.0	29.4
247	46.3	78.3	20.5	10.4	3.15	112.35	114.0	....
390	27.5	49.8	6.15	2.30	1.05	59.30	61.8	63.3
345	41.2	53.15	7.10	2.45	1.25	63.95	67.8	68.2
397	29.0	36.8	5.4	2.05	0.3	44.55	49.0	50.3
398	27.2	36.65	4.05	1.15	0.25	42.10	50.1	50.6
333	31.3	61.1	11.8	5.1	1.6	79.60	86.0	86.8
334	16.0	33.9	4.25	1.95	0.2	40.30	46.8	48.2
236	33.6	58.9	10.1	3.55	1.85	74.40	81.0	81.4
237	10.8	35.75	5.1	2.9	0.5	44.25	45.4	46.8

TABLE 11

Exchangeable bases present and found by the proposed method

EXCHANGEABLE BASE	M.E. PER 100 GM.	
	Present	Found
Ca	33.8	34.6
Mg	10.5	11.0
Na + K	7.0	5.2

The difficulty of replacing exchangeable Ca by any of the usual reagents employed for this purpose and the ease with which this can be accomplished by precipitation *in situ* suggest a very simple method of estimating all the exchangeable bases in non-calcareous soils. The method is based on the fact that *all other bases except Ca are replaced by a single treatment with normal ammonium acetate.* The following is a detailed description of the method:

Twenty-five grams of soil is shaken for 1 hour, or left for 4 hours with frequent stirring, with 250 cc. of 0.05 *N* to 0.1 *N* oxalic acid in normal ammonium acetate. The suspension is then filtered through a dry filter paper. Fifty

to one hundred cubic centimeters of the filtrate is titrated with standard permanganate or precipitated with $CaCl_2$, if the filtrate is colored, as described in the foregoing. The total decrease in the concentration of oxalate ion is equivalent to the exchangeable Ca in 25 gm. of the soil. Another 100 to 150 cc. of the filtrate is evaporated to dryness in a porcelain dish and ignited to convert Na, K, and Mg acetates or oxalates into carbonates. The ignited residue is taken up with 50 per cent alcohol, which dissolves Na and K carbonates, leaving behind Mg carbonate. The alcoholic filtrate is evaporated to dryness and titrated for Na and K carbonates by first adding excess of standard acid. The residue of Mg carbonate is titrated separately by adding excess of standard acid, boiling, and back titrating with standard alkali. These titration values give the amount of exchangeable Na + K and of Mg per 10 gm. of soil for every 100 cc. of the filtrate.

The foregoing method was tested on an acid treated soil to which known amounts of Ca, Mg, Na, and K were added as hydroxides. The results given in table 11 show a good agreement between the bases present and those found by the proposed method.

SUMMARY

A simple method of estimating exchangeable Ca and other bases in non-calcareous soils is described. It consists in shaking a known weight of the soil with 0.1 *N* oxalic acid in *N* ammonium acetate. In this way the whole of the Ca is precipitated as oxalate, and the decrease in the concentration of the oxalate ion is equivalent to the exchangeable Ca in the soil.

Under the experimental conditions described, all the exchangeable bases other than Ca pass into solution as acetates or oxalate. A known volume of the filtrate is evaporated to dryness and ignited, when these bases are obtained as carbonates and are determined by titration with standard acid.

A DEVICE FOR MEASURING PRECIPITATION WATERS LOST FROM THE SOIL AS SURFACE RUNOFF, PERCOLATION, EVAPORATION, AND TRANSPIRATION

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The investigations which are now in progress on the movement of surface waters and their effect upon the problem of conservation of both soil and water have pointed toward the need of certain types of studies. Among these is the need for specific information, developed under as nearly normal conditions of exposure as possible, upon the relationship of surface runoff to water absorption and retention by the soil. That portion of the precipitation which is retained by the soil under various conditions of treatment as well as for soils of various physical characteristics is water not only passed beyond the possibility of causing erosion, but further, is largely water which is of potential value to crop growth. The fact that many treatments may increase the absorption of precipitation waters is well known. The quantitative relationships between rate of precipitation, rate of infiltration, and rate of runoff are less well known. Such information is needed for soil series and types as well as for various conditions of treatment of each.

To be of practical use and true value any such quantitative measurements must be based upon soil of normal field structure, since a disturbance of such structure results in very abnormal infiltration rates. This fact has become recognized in the various improvements in design of lysimeters in recent years.

In many of the early established lysimeters either one or both of two serious defects existed:

a) The soil was filled in after screening or other preparation such that original field structure was destroyed; and/or

b) Free runoff of surface waters was not permitted.

Both of these conditions, of course, have the effect of increasing the quantity of water which passes through the soil profile, the result being not only to give abnormally high quantitative results but also to upset differential effects between treatments. Those soil treatments which normally would retard water absorption do not show a true relationship to other treatments under conditions in which all of the precipitation is retained upon the area of the lysimeter, thereby enforcing similar or nearly similar absorption rates.

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McCall and Bower (3) encased in tanks blocks of soil of undisturbed structure. These blocks were 3½ feet square by 4 and 6 feet deep, respectively. Corn was grown on the tanks, and tarred paper frames were used to cover the plant and protect from rainfall. Each tank was equipped with a syphon to maintain a constant groundwater table, and water losses from this table were measured in comparison with losses from an open water tank similarly equipped with a syphon and located nearby.

Duley (1) has described a type of lysimeter which permits the study of large sections of soil of undisturbed structure. This lysimeter consists of a heavy galvanized cylinder with removable bottom. A column of soil is trimmed to size and the cylinder placed over the column, the bottom fitted and the entire mass moved to the place of final installation. No provision for free surface runoff was made, although it appears that such could readily be permitted without fundamental change in design of the equipment.

Joffe (2) has described the Russian type of lysimeter which largely overcomes the two objections already enumerated. This type of lysimeter provides the essentials both of free runoff and soil of normal structure. It does not, however, permit the measurement of runoff in relation to percolation. Furthermore, as Joffe points out with reference to the relatively impervious B horizon, "the vertical movement of moisture becomes impeded and horizontal movement along this horizon sets in, a phenomenon to be reckoned with in lysimeter studies." Hence the percolation may not be quantitatively related to either precipitation or surface runoff where an impervious horizon is under study.

Weaver and Crist (4) have determined by direct measurement the loss of water from vegetation without disturbing the normal structure of the soil. For this purpose a cylinder 3 feet long and with an inner cross-sectional area of 1 square foot was forced over the grassy vegetation and into the soil, the exterior soil being pared away as the cylinder was forced downwards. These cylinders of soil were then removed and after being weighed were placed in a trench where the bottoms were sealed. The trenches were then filled with soil, and the surface sod was restored. Water losses over a 15-day period were calculated by weighing.

In order to provide a means of quantitative study of percolation and runoff in relation to rainfall the equipment described herein has been designed and constructed. Six lysimeters of this type have been in operation at the Soil Erosion Station at Temple, Texas, for approximately 4 years, and twelve of the same general type but with minor improvements have been in operation at the Clarinda Iowa Station for approximately 2 years. The general design, therefore, has been subjected to considerable practical experience with such satisfactory results that additional installations have lately been made.

The plan and elevation of the equipment is given in figure 1. The cylinders of this equipment as now installed are each 3 feet in diameter and 3 feet in depth, and contain nearly one ton of soil. They were filled with soil in practically undisturbed structural condition in the following manner: A suitable location was first selected, having uniform soil which was typical of the soil used in supplementary runoff experiments (in this case a Marshall silt loam having a surface horizon approximately 12 inches deep). The uniformity of the soil was determined by careful examination of the profile of a trench dug on four sides of the proposed location of the cylinder.

The cylinder was set in a vertical position by careful leveling and forced to its full length into the soil by means of three house-jacks actuated from above by suitably weighted scaffolding (pl. 1, fig. 1). Approximately 6,000 pounds of sand bags were required to supply the necessary weight for forcing this

cylinder into the 3-foot profile. During this operation a heavy iron ring was bolted securely approximately 4 inches above the base of the cylinder to maintain it as nearly as possible in a true circular form. While the cylinder was

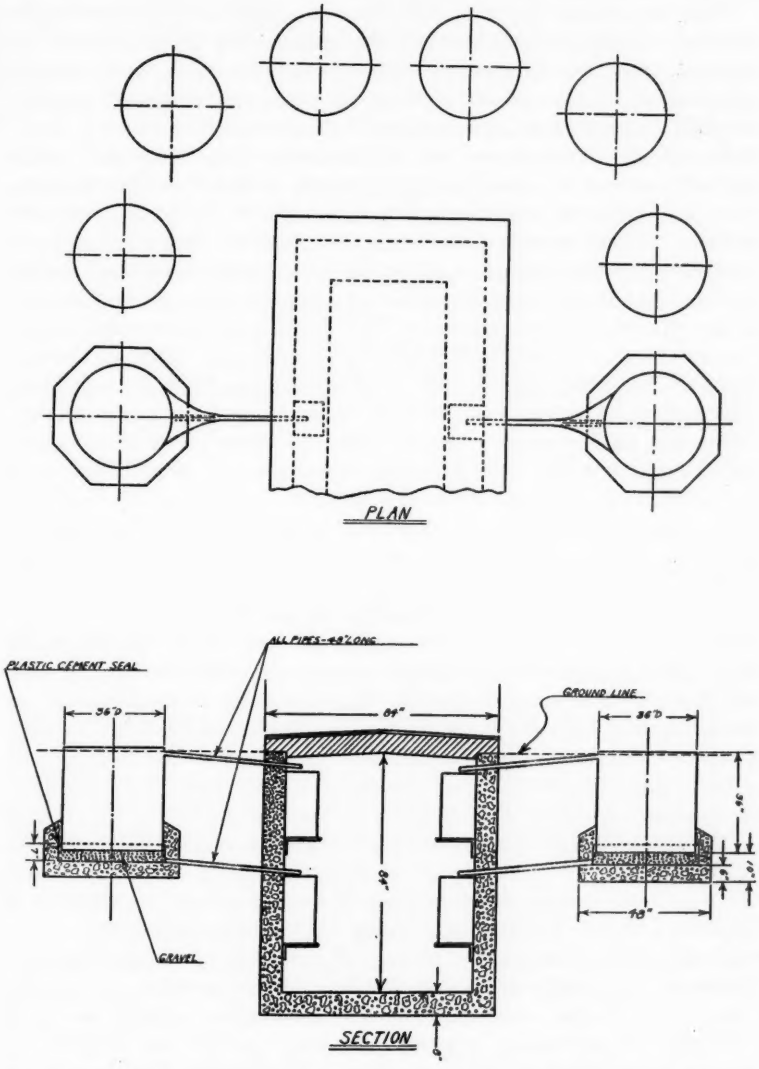

FIG. 1. PLAN AND ELEVATION OF EQUIPMENT USED IN THE MEASUREMENT OF SURFACE RUNOFF AND PERCOLATION FROM SOIL COLUMNS OF UNDISTURBED STRUCTURE

being forced downward the exterior soil was gradually removed to within a few inches of the bottom level of the cylinder. At the same time a series of six samples were obtained around the perimeter for each 6 inches of depth, making a total of 36 samples for each cylinder.

When the cylinder had been fully sunk excavation was continued on its exterior to a depth approximately 1 foot greater, and the lower hoop was removed, hooks were attached to the lower extremity (pl. 1, fig. 2), and the mass was supported on a hoist while the soil column was severed and carefully trimmed to an exact line coinciding with the plane of the lower end (pl. 1, fig. 3). When this operation is done on soil of this character (high silt or clay content and without rock or stone) at approximately optimum moisture content, there is no difficulty in retaining the entire mass of soil in the open-ended cylinder. At the same time the cylinders of soil were being prepared bases for their support in the final location were being constructed in the following manner: A reinforced concrete slab having a diameter 1 foot greater than that of the cylinder was first constructed. On this slab was then placed the pan which was to serve as the bottom of the completed cylinder. This pan, having a depth of 7 inches and diameter of 40 inches, was filled to a depth of 4 inches with coarse gravel which had been previously washed with hydrochloric acid and finally with distilled water. Above this layer of coarse gravel a layer of fine gravel similarly washed was then placed and tamped into position so that its surface was level. The pan itself was adjusted to have a 1-inch fall toward the outlet, which consisted of a 1-inch pipe set in the lower rim of the pan. A slight depression across the pan had been formed during its construction for the purpose of further aiding the movement of water to the outlet.

The cylinder of soil was then moved to the final location and placed carefully upon the pan. The joint between the pan and cylinder was first sealed by means of a preparation of asphalt, asbestos, and silica (pl. 2, fig. 1), after which a reinforced concrete shoulder was constructed in a manner to join firmly together the base and the cylinder as a single unit (pl. 2, fig. 2). The completed structure has such strength that the entire mass including pan and cylinder might be moved without breakage if desired, although this operation is, of course, not necessary (pl. 2, fig. 3).

The method of forcing the cylinder into the soil is such as to preserve the original vegetation and the original soil slope (pl. 3, fig. 1). Finally, however, the slope may be adjusted by fractions of an inch as may be necessary to duplicate precisely the slope in adjoining supplementary experiments.

In the completed installation (pl. 3, fig. 2) surface outlets care for the movement of surface runoff, which is carried into suitable containers in a nearby cellar. Likewise, percolate is piped from the gravel pan to suitable containers.

During the construction operation the cylinders of soil were weighed, the volume was measured, the moisture content was determined, and the apparent specific gravity of the mass was calculated. Detailed chemical and physical analyses of the soil have been made.

In the final installation the rain gage is installed in a manner such that its

top extends above the surface of the soil to the same height as that of the cylinders. Experience has demonstrated this to be necessary, inasmuch as records from rain gages with their tops extended 5 feet above the ground are rather consistently different from records of rain gages with their tops nearer the plane of the soil surface.

The data are handled in the following manner: The rainfall is carefully measured and calculated in terms of cubic centimeters per cylinder. Percolate is regularly measured and recorded as cubic centimeters, and in the surface runoff the soil and water are separated and each is separately calculated—the water in terms of cubic centimeters and the soil in terms of grams. Since over a period of time the cylinders of soil can neither continuously increase nor continuously decrease their content of soil water, it is feasible at the close of a selected period to calculate the disposition of the precipitation waters as they may occur in the form of evaporation and transpiration, as well as to

TABLE 1

Disposition of Precipitation Waters

May 1, 1933–May 1, 1934; Precipitation 25.15 inches

	FALLOW	FALLOW PLUS O.M.*	CORN	CORN PLUS O.M.*
Runoff, surface, *inches*	6.8170	6.3028	4.2729	2.5175
Percolation, surface, *inches*	4.1193	5.1770	0.7624	1.5122
Evaporation, surface, *inches*	14.2137	13.6702		
Evaporation plus transpiration, surface, *inches*			20.1147	21.1203

* The fallow plus organic matter and the corn plus organic matter treatments each receive annually in early May an application of well-rotted stable manure at the rate of 16 tons per acre.

determine directly that amount lost as surface runoff and as percolate. This is done as follows:

On cropped cylinders:

$$E + T = P - (M + R)$$

where: E = Evaporation from the soil surface
T = Transpiration from the plants grown in the cylinders
P = Precipitation
M = Percolate from the cropped cylinders
R = Surface runoff from the cropped cylinders.

If the transpiration ratio for the type of plant is known, then the total transpiration for the season may be calculated and the soil evaporation may be determined from the equation:

$$E = P - (M + R + T)$$

On fallow cylinders:

$$E = P - (M' + R')$$

where: M' = Percolate from the fallow cylinders, and
R' = Surface runoff from the fallow cylinders.

A simple total of the results for a calendar year from triplicate treatments is given in table 1.

There are at present in operation at the Soil Erosion Experiment Station in Iowa 24 units providing a total of 8 different treatments, each in triplicate and including two different soil types which receive corresponding applications of organic matter. The detailed data from this study are being reported separately.

A number of special advantages are found in this equipment whether its primary purpose be erosion research or whether for the usual lysimeter studies. For the latter purpose normal percolation rates are provided by this type of installation, whereas in the more commonly used type of lysimeter abnormal percolation occurs. This is due to the fact that where all of the precipitation waters are forcibly retained upon the soil surface such waters must ultimately enter into the soil, enforcing a rate of percolation in excess of that occurring under corresponding field conditions. Such differential effects are particularly pronounced in the case of those treatments which have a deflocculating effect upon the soil. In the Russian type of lysimeter, where free surface runoff is permitted, percolation rates for permeable soils are probably close to normal. In the case, however, where a relatively impermeable horizon intervenes there is no surety in the Russian type lysimeter that water from outside of the measured area may not enter into the measurement of the percolation.

Both the Russian type and that type of lysimeter described in the foregoing have the advantage of permitting studies on soil of undisturbed structure. In many types of studies it is very desirable to be able to relate quantitatively percolation and surface runoff to the precipitation. This advantage, as well as that of the indirect calculation of vapor losses, is obvious, and the equipment described is adaptable to the purpose.

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PLATE 1

FIG. 1. Method of sinking cylinder into selected soil area. Jack screws were used for this purpose to give a slow, even movement without jarring the soil column. The cylinder was maintained exactly perpendicular throughout the operation.

FIG. 2. Two cylinders sunk to full depth, one of which has hooks attached ready for fastening to hoist.

FIG. 3. Gravel pan in position upon base. Note cylinder of soil on hoist ready to be moved into position upon base.

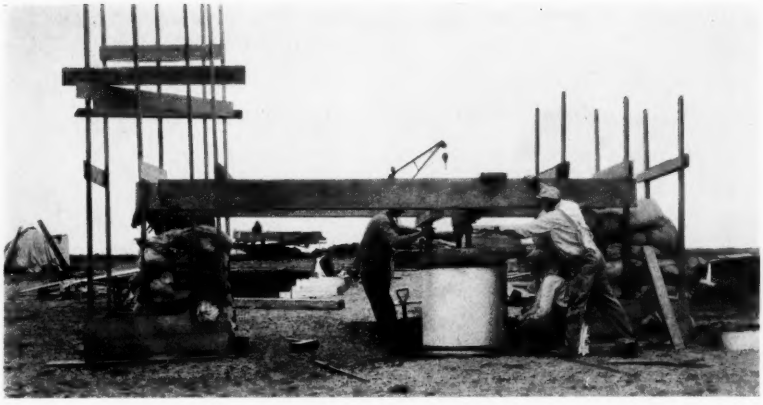

FIG. 1

FIG. 2

FIG. 3

PLATE 2

FIG. 1. The cylinder in position upon the gravel pan and the operation of sealing a joint between the pan and cylinder with a preparation of silica, asphalt, and asbestos.

FIG. 2. Reinforcement in position for constructing concrete shoulder about base of cylinder and including pan. Also a view of one such base complete.

FIG. 3. Four cylinders in position, with the completed base.

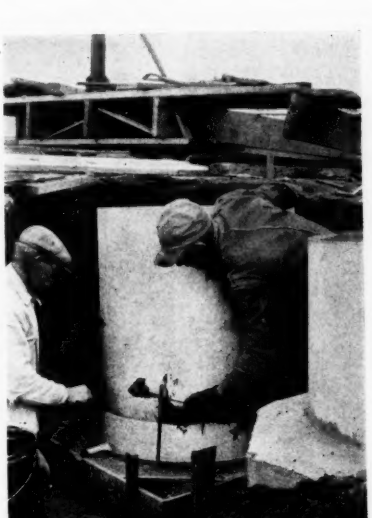

FIG. 1

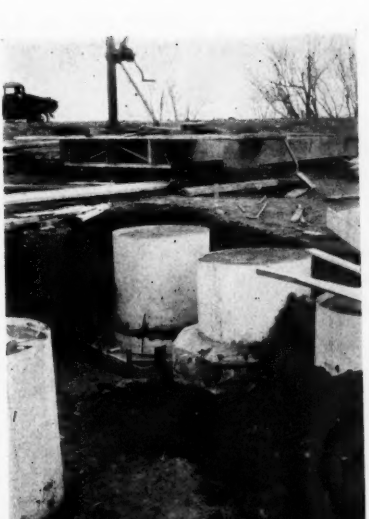

FIG. 2

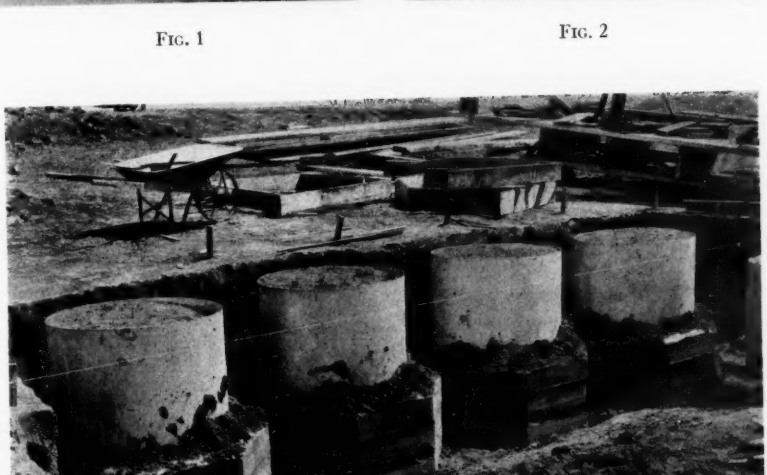

FIG. 3

PLATE 3

FIG. 1. Undisturbed condition of soil in cylinder after being sunk to its full depth. The original vegetation and the original soil slope remain.

FIG. 2. Cylinders spaced equi-distant from one another and from central cellar. (a) outlet pipe for surface runoff; (b) rain gage; (c) cellar housing measuring equipment for runoff and percolate.

FIG. 1

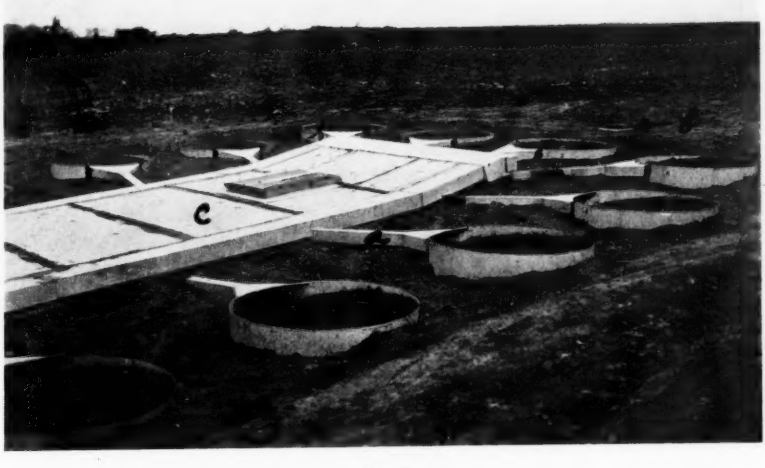

FIG. 2

SORPTION OF LIQUIDS BY SOIL COLLOIDS: II. SURFACE BEHAVIOR IN THE HYDRATION OF CLAYS

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In previous investigations (14) the authors have shown that the sorptive behavior of different soil colloids is related to the structure of the colloidal complex, to the amount and nature of the ions adsorbed on the surface, and to the electrical properties of the molecules of the sorbed liquid. It is the purpose of this paper to discuss the rate of water sorption by colloidal clays and such properties of clay-water systems as viscosity, charge, hygroscopicity, heat of wetting, and swelling, in order to permit a clearer concept of the rôle of surface behavior in the hydration of colloids.

EXPERIMENTAL PROCEDURE

Water sorption and swelling were measured as discussed in Part I (14). Viscosities were determined with a special form of Oswald viscosimeter which permitted measurements in a closed system at higher temperatures. Preliminary observations showed no influence on the viscosity data by pressure variations within the systems from ½ to 2 atmospheres. Heat of wetting data were obtained with a Bunsen ice calorimeter. The contraction of the ice-water system was measured in a horizontal capillary which was installed at such a relative height to the bulk of the water and mercury as practically to eliminate any movement of the mercury due to melting or freezing of water induced by either pressure or suction. The reproducibility of the caloric data was within 5 per cent. The clays were pulverized, dried for 3 days at 110°C., and then kept over P_2O_5. Before being placed in the ice calorimeter they were cooled for an hour in an ice-water bath. Hygroscopicities were measured as usual over $H_2SO_4 - H_2O$ mixtures. The charge and dispersity data are those reported by Lutz (10).

DISCUSSION OF RESULTS

The rate of water sorption.—The rates of water intake by different colloidal systems are shown in tables 1, 2, and 3. The data in table 1 point out quite

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clearly that the sorption of water by Li- and Na-saturated colloids is a more complex phenomenon than in the case of the K-, Ba-, Ca-, and H-systems. Sorption by the latter systems was 70–75 per cent complete within 1 minute and 85–90 per cent finished in 10 minutes. The pores were filled with easily expressible free water. The sorption of water by the Li- and Na-clays was not complete after 3 days. Of the total amount taken up during that time only 15 per cent was imbibed during the first minute and 22 per cent during the first 10 minutes. After about 24 hours the colloids began to disperse in the sorbed water and to diffuse through the porous filter plate. Consequently,

TABLE 1

Rate of water intake by Putnam colloid saturated with different cations

TIME	WATER INTAKE PER GRAM COLLOID					
	Li*	Na*	K	Ba	Ca	H
minutes	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
1	0.960	0.810	1.120	1.344	1.362	1.330
5	1.195	1.020	1.230	1.480	1.540	1.506
10	1.360	1.200	1.284	1.526	1.624	1.566
20	1.615	1.490	1.316	1.564	1.678	1.588
30	1.765	1.555	1.326	1.584	1.704	1.608
120	.....	.....	.....	1.634	1.778	1.676
150	2.575	2.255	1.372	.....	.....	.....
1080	.....	.....	.....	1.688	1.888	1.780
1140	4.130	3.700	1.456	.....	.....	.....
1200	4.195	3.725	1.458	.....	.....	.....
1440	4.440	3.940	1.464	1.750	1.908	1.790
1550	4.510	3.975	.....	.....	.....	.....
4050	6.125	5.240	.....	.....	.....	.....
4320	6.225	5.270	.....	.....	.....	.....
Pore space, cc./gm.....	1.250	1.250	0.960	0.900	1.000	0.98
Swelling, cc./gm.....	4.975	4.020	0.504	0.850	0.908	0.81

* The end values for the Li- and Na-collids are somewhat too low, since diffusion of these colloids through the porous filter plate started at about 24 hours. Sorption of water resulted in complete dispersion.

the end values for sorption are undoubtedly too low. It should be noted that although suspensions of Li-, Na-, and K-clays are dispersed to approximately the same extent, the K-saturated systems take up water in a similar manner to those saturated with H, Ba, and Ca ions. The data in table 2 show that although the amount of water sorbed by different H-clays varies with the nature of the colloid, the rates of sorption are of the same order of magnitude.

Sorption studies with colloidal bentonite systems showed (table 3) that the rate of water intake was much slower than with clays but that sorption extended over a much longer period of time. The quantity of water imbibed per gram of bentonite was much greater than per gram of clay. Equilibrium

with clay systems was obtained within 1 to 3 days; bentonite, however, continued to sorb small amounts of water after 5 to 7 days. All bentonite systems assumed a jelly-like consistency during the process of imbibition as compared with the dispersed condition of Li- and Na-clays and the seemingly granular nature of the K-, Ca-, Ba-, and H-clays. With the clay systems, the K-satu-

TABLE 2

Rate of water intake by various colloidal clays saturated with hydrogen ions

TIME	WATER INTAKE PER GRAM COLLOID			
	Lufkin	Wabash	Susquehanna	Cecil
minutes	*cc.*	*cc.*	*cc.*	*cc.*
1	1.56	1.249	1.212	1.106
5	1.64	1.520	1.382	1.154
10	1.68	1.554	1.418	1.168
30	1.72	1.618	1.490	1.186
60	1.76	1.640	1.526	1.206
180	1.80	.....	1.578	1.234
1140	....	1.828	1.666	1.294
1440	2.00	1.838	1.666	1.294
Pore space cc./gm.....	0.82	0.90	1.10	1.24
Swelling cc./gm.....	1.18	0.938	0.566	0.054

TABLE 3

Rate of water intake by bentonite saturated with various cations

TIME	WATER INTAKE PER GRAM BENTONITE					
	Li	Na	K	Ba	Ca	H
minutes	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
10	0.820	0.970	1.525	2.895	.....	2.645
20	1.190	1.310	.....	2.975	2.985	2.730
30	.....	.....	.....	3.015	3.025	2.765
60	1.910	2.090	2.625	3.085	.....	2.830
120	2.640	2.860	3.315	.....	3.215	.....
1440	7.430	7.695	7.145	3.475	.....	3.210
4320	11.170	11.290	9.055	3.830	3.920	3.570
5760	12.125	12.280	9.755	3.900	4.000	3.650
Pore space cc./gm.....	1.350	1.200	1.200	1.400	1.500	1.450
Swelling cc./gm....	10.775	11.080	8.555	2.500	2.500	2.200

rated colloid behaved like the divalent clays; with bentonite, the Li, Na, and K ions exerted similar effects upon the sorption of water.

The differences in the rates and amounts of water sorption by these various colloidal systems indicate that the structure of the particles and the nature and activity of the colloidal surfaces must play important rôles in this type of

hydration. The significance of these results will be more thoroughly discussed under the subject of swelling.

Hydration of clays.—It is known from fundamental colloid chemistry that charge and hydration are the two factors governing the behavior of colloidal suspensions. For truly non-hydrated suspensoids (gold sols), charge plays the predominant rôle; for hydrated emulsoids (gelatin sol), hydration is more important. Experimental data have proved that colloidal aluminosilicates have properties common to emulsoids and suspensoids. The hydrophilic character of aluminosilicates is usually more pronounced the higher the SiO_2-sesquioxide ratio of the colloid; colloids with a low ratio tend to have hydrophobic characteristics. It should be expected that in highly hydrated aluminosilicate systems the influence of charge, as derived from the zeta-potential, on dispersion and the properties of the system relating thereto will be small as compared with the effect of the hydration factor. Consequently, in highly hydrated bentonite systems where the diffuse electrical double layer is undoubtedly thicker than in the less hydrated clays, the nature of the exchangeable cations in the somewhat mobile outer layer should not have such pronounced effects on dispersity. Moreover, the influences of the ions in the outer layer on the hydration of bentonite and clay surfaces should not be expected to be exactly similar. The experimental results of Lutz (10) and Marshall (11) on the charge of colloidal particles and dispersity as summarized in table 4 indicate quite clearly such differences in the effects of the exchangeable cations on clays and bentonites. It should be noted that the stability of the bentonite sols as measured by their degree of dispersion is nearly the same, irrespective of the nature of the ion on the exchange complex. Ca-, Ba-, and H-bentonites are as stable as the Li-, Na-, and K-systems. Only the Li-, Na-, and K-Putnam clays are permanently stable; the H-, Ca-, and Ba-clays undergo slow coagulation. The bentonites are from 5 to 7 times more highly hydrated than the various Putnam clays.

These data also show that the effect of the zeta-potential of different clays on their stability is determined to a large extent by the degree of hydration of the clay. For example, the potentials of the Davidson and Putnam colloids that are saturated with the alkali cations are practically the same. The Davidson colloids, however, flocculate rapidly, whereas the Putnam systems are stable. Undoubtedly as the degree of hydration of the surface increases the probability of adhesion for any given potential becomes smaller.

Many data have been assimilated in this study to show the differences in hydration of the various colloidal systems. Relative hydration of these colloids has been approached from the points of view of the adsorption of water molecules from the vapor phase (hygroscopicity), the adsorption or orientation of water molecules in the presence of an excess of water (relative viscosity), the intake of water from a free water surface (sorption and swelling), and the energy relationships associated with the wetting of a dry surface (heat of wetting).

The relative hydration of each of the different colloidal suspensions was calculated by means of the modified Einstein equation

$$\eta_r = \frac{1 + 2.5\phi}{1 - \phi}$$

where η_r = relative viscosity = $\frac{\text{viscosity of suspension}}{\text{viscosity of water}}$

ϕ = volume in per cent of suspended particle with hydration hull.

Subtraction of the volume of the solid soil particle from ϕ gave the amount of hydration. It was fully realized that, in view of the theoretical incompleteness of the Einstein formula as well as the increase in viscosity due to aggregation phenomena, the evaluation of the viscosity data in terms of hydration of the colloidal particle must be made with proper interpretations. It is believed, however, that if suspensions with equal dispersions are used the hydration values calculated from viscosity measurements will give satisfactory comparative data as to the amount of water bound to the colloidal surfaces.

Data relative to the hydration of several colloidal suspensions are summarized in tables 4, 5, and 6. The hydration values in table 4 show that colloidal bentonite suspensions are much more highly hydrated than colloidal clays. These results also show that flocculation phenomena may lead to misinterpretation of the viscosity measurements in terms of hydration, since the flocculated Davidson colloids exhibit higher hydration than the Putnam colloids. Other hydration studies such as swelling and hygroscopicity show, without doubt, that the Putnam clay systems are more highly hydrated. The similarity in the hydration of the H-, Ca-, and Ba-Putnam clays and of the Li- and Na-clays is due to the slow coagulation of the former.

The values in tables 5 and 6 indicate the effect of exchangeable cations on the hydration of Putnam and Wabash clays. It is seen in the case of the Putnam system that the ratio of hydration in an excess of water (from viscosity measurements) to that in an atmosphere of water vapor (hygroscopicity over 30 per cent H_2SO_4) is almost constant for all ions.

The colloid appears to be about 30 times more hydrated in suspension. The hygroscopicity data, obtained by the common procedure of keeping the clay for 3 days in a dessicator over 30 per cent H_2SO_4, obviously do not represent true equilibria. This has already been shown by Deluc (3), and has been emphasized by Katz (8). Therefore, it cannot be decisively concluded from these data that only about one-thirtieth of the water attracted by a suspended colloid is held by a force greater than the avidity of 30 per cent sulfuric acid for water. The constancy of the hydration-hygroscopicity ratio rather points to an identity of the water-binding forces for both phenomena. The lower speed of water adsorption from an atmosphere can easily be conceived as being due to the low concentration of water molecules in the vapor and the resulting small number of those striking the colloidal surface per unit time.

Since a certain time element is needed for the orientation and binding of these water molecules there seems to be a greater probability for the orientation of relatively slow associated water molecules than for the orientation of the faster H_2O molecules from the atmosphere during their relatively small striking time.

Hydration as calculated from the viscosity of aqueous suspensions is related to the energy of adsorption as measured by the heat of wetting. For the Putnam colloid the hydration-heat of wetting ratio is about 0.43 for Li-,

TABLE 4

Relation of charge and hydration in different colloidal systems

COLLOIDAL SYSTEM	ZETA-POTENTIAL (LUTZ-REITEMEIER)	WATER OF HYDRATION* (WINTERKORN) (LUTZ)	DISPERSITY	
			Flocculation time (Lutz)	Particles <100 mμ (Marshall)
	millivolts	*cc./gm.*		*per cent*
H-Davidson	36.8	6.66†	1 min.	
Li-Davidson	40.5	9.01	2 min.	
Na-Davidson	39.4	8.06	2 min.	
K-Davidson	37.9	11.41	2 min.	
Ca-Davidson	36.3	5.11	1 min.	
Ba-Davidson	35.3	5.76	1 min.	
H-Putnam	36.3	5.20	3 days	37.4
Li-Putnam	40.3	5.25	Stable	60.1
Na-Putnam	38.5	5.25	Stable	62.2
K-Putnam	38.7	4.07	Stable	56.3
Ca-Putnam	35.0	5.20	3 days	4.9
Ba-Putnam	32.6	5.20	3 days	24.4
H-Bentonite		35.00	Stable	34.0
Li-Bentonite		28.40	Stable	37.8
Na-Bentonite		24.10	Stable	35.2
K-Bentonite		21.30	Stable	35.7
Ca-Bentonite		24.20	Stable	31.2
Ba-Bentonite		34.00	Stable	31.9

* From viscosities.

† Partly flocculated.

Na-, and K-systems, even though the K ion causes a lower heat of wetting and a lower viscosity. This ratio is 0.38 for the H, Ca, and Ba ions. The data strongly suggest that this hydration is a function of the energy of adsorption. If the ratio of swelling to heat of wetting is considered, it is observed that this value for H-, K-, Ca-, and Ba-systems is about 0.06; that for the Li- and Na-colloids is around 0.43. Swelling water in the latter systems approaches the amount of hydration calculated from the viscosity of the colloids in aqueous suspension. This should be expected from the aforementioned behavior of these clays in the sorption apparatus.

In the case of the Wabash colloid, which contains a considerable amount of organic matter, the hydration-heat of wetting ratio of the Ca- and Ba-systems is of the same order as the Putnam clays. The Li-, Na-, and K-saturated colloids, however, exhibit a much greater hydration as compared with the heat of wetting, causing the hydration-heat of wetting ratio to be higher.

TABLE 5

Hydration of Putnam colloid

COLLOIDAL PROPERTY	NATURE OF CATION					
	H	Li	Na	K	Ca	Na
pH	4.1	7.61	7.66	7.32	6.96	6.86
Hydration*, cc./gm.	5.20	5.25	5.25	4.07	5.20	5.20
Swelling, cc./gm.	0.81	4.97	4.02	0.50	0.91	0.85
Heat of wetting, cal./gm.	13.6	12.0	12.0	9.5	15.0	13.9
$\frac{\text{Swelling}}{\text{Heat of wetting}}$	0.06	0.414	0.335	0.053	0.061	0.061
$\frac{\text{Hydration*}}{\text{Heat of wetting}}$	0.382	0.437	0.437	0.429	0.382	0.381
$\frac{\text{Hydration*}}{\text{Hygroscopicity (30 per cent } H_2SO_4)}$	28.65	30.65	31.75	31.9	31.9	29.9

* From viscosities.

TABLE 6

Hydration of Wabash colloid

COLLOIDAL PROPERTY	NATURE OF CATION					
	Li	Na	K	Ba	Ca	H
Hydration*	7.39	7.45	7.03	6.67	6.74	Floc.
Swelling	3.10	3.73	0.55	0.74	0.79	0.94
Heat of wetting	11.4	11.6	8.9	14.9	15.3	13.9
$\frac{\text{Hydration*}}{\text{Heat of wetting}}$	0.648	0.643	0.789	0.448	0.440	.....
$\frac{\text{Swelling}}{\text{Heat of wetting}}$	0.272	0.322	0.062	0.052	0.049	0.067

* From viscosities.

This greater hydration is undoubtedly due to the influence of the alkali ions on the organic colloids present.

Apparently there are at least two ways in which water can be associated with colloidal particles, not taking into consideration mechanically occluded water. Water molecules may be oriented at the surface as a result of the electrical properties of both the liquid and the surface. Water may also be adsorbed because of osmotic effects, as described by Proctor, Proctor and Wilson, and Mattson. The first process is associated with the release of an

appreciable amount of heat and will be referred to as "hydratation." The osmotic type of hydration does not take place with the liberation of measurable quantities of heat. It apparently plays a significant part in the hydration of the alkali-saturated organic colloids in the Wabash clay. This osmotic hydration is not restricted to organic colloids but is also found, as Mattson (12) has shown, in highly hydrated aluminosilicates such as bentonites.

The observations of Marshall (11), Lutz (10), Winterkorn (14), Janert (6), Mattson (12), and others suggest that the water association with common colloidal clays is principally due to hydratation; that of organic colloids and bentonites also includes an appreciable amount of osmotic hydration. Hydratation can be pictured as oriented adsorption of water molecules at the surface of the colloid and around the ions whereby the exchangeable ions are found either in conformity with the surface or very close to it.

In the osmotic type of hydration the hydratated ions surround the hydratated surface in a diffuse layer. These ions keep within a distance from the surface in which the mean osmotic force is in equilibrium with the mean electric attraction due to the different charges of the colloidal surface and the exchangeable ions. The apparent volume of the colloidal particle is then defined by the extent of the ionic atmosphere. The free water in which the cations are dispersed is naturally an integral part of the apparent volume of the swollen particle, and since the diffuseness of the double layer is a function of the osmotic pressure of the cations this type of swelling has been termed "osmotic." It will be understood now that this type of swelling is not directly connected with any appreciable energy change in contrast to hydratation. The diffuseness of the ionic atmosphere is also a function of the electric structure of the colloid surface. There seems to be reason to believe that a study on the polarizing effect of the crystal surfaces of the different soil colloids will throw light upon the problem of the different behavior of bentonites and clays.

It can be stated, therefore, in colloid chemical terms that the nature of the inner layer and its effect on adsorption of ions and water molecules determine to a great extent the character and amount of hydration in aqueous clay systems. The kind of ion adsorbed on the surface plays an important rôle in hydratation as well as in the osmotic type of hydration. This rôle, however, is probably not so simple and well-defined as to make the heat of wetting of clays always a definite fraction of the heat of hydration of the ions in the surface. These relationships will be discussed later in this paper.

In order to obtain information concerning the force with which water is oriented or held around a colloidal particle, the effect of temperature on the viscosity and hygroscopicity of colloids was studied. The data in tables 7 and 8 show that an increase in temperature, which correspondingly causes an increase in the kinetic energy of the water molecules, produced marked decreases in the hydration of the particles as calculated from viscosity and hygroscopicity data. At temperatures close to the boiling point of water the colloid is only about 50 per cent as highly hydrated as at room tempera-

ture. This decrease in hydration was a uniform function of increasing temperature, since there were no abrupt changes in temperature-hydration curves. The hygroscopicity data show that increasing the temperature from 30° to 40°C. caused over a 50 per cent decrease in the amount of water ad-

TABLE 7

Hydration of Putnam and Wabash colloids as affected by temperature*

TEMPERATURE	HYDRATION, CC. H_2O PER GRAM COLLOID					
	Li	Na	K	Ca	Ba	H
			Putnam colloid			
°C.						
30	5.25	5.25	4.07	9.75	5.04	5.20
50	3.73	4.56	3.56	3.90	3.73	3.52
70	2.52	2.53	2.34	1.98	2.87	2.16
99	2.34	2.52	2.16	0.86	2.16	2.70
			Wabash colloid			
30	7.39	7.45	7.03	6.74	6.67	17.95
50	6.37	6.29	6.22	6.14	6.22	16.08
70	5.01	5.09	4.75	6.44	4.40	14.79
99	3.86	3.67	3.39	7.10	3.39	9.70

* From viscosities.

TABLE 8

Water adsorption by different aluminosilicates as a function of temperature

Vapor pressure = 30 mm. Hg, relative humidity = 94 per cent at 30°

COLLOID	H_2O ADSORBED			
	Temperature			
	30°	40°	50°	80°
	per cent	*per cent*	*per cent*	*per cent*
H-Bentonite	32.7	13.0	7.51	2.12
H-Putnam	25.8	10.8	5.7	2.3
H-Davidson	21.4	3.5	2.6	1.2
H-Permutite	28.4	16.9	4.9	3.1
Strength of H_2SO_4–H_2O mixture used to maintain constant humidity, *per cent*	10	41.5	52.75	68.75

sorbed, even though the water vapor pressure was held constant. These results, in conformity with the previous discussions on hygroscopicity and hydration, indicate that the water molecules in the outer layers of the water shell of a soil colloid in aqueous suspension are held by relatively small forces, smaller than the water attractive forces of the sulfuric acid used in the hygro-

scopicity determinations. The data for the hydration as calculated from the viscosities were somewhat affected by coagulation phenomena at the higher temperatures, but not sufficiently to account for the characteristic difference between the temperature function of hydration and that of hygroscopicity. This difference may be due in part to different equilibria between the clay, on one hand, and molecular or associated water, on the other.

Swelling of soil colloids.—In Part I of this study the swelling of soil colloids has been considered as the difference between the sorption of water and of an inactive, non-polar liquid such as CCl_4. It is realized, in the light of the different physical behavior of the swollen systems, that the apparent swelling does not represent any one specific physical or physicochemical phenomenon. In the hope of clarifying many of the existing and apparently contradictory explanations of swelling, the data obtained in this study on the swelling of colloidal aluminosilicates will be discussed from the points of view of the different interpretations usually given to the swelling process.

At the end of the last century the botanists defined "swelling" as the intake of liquid by a solid body, whereby the volume of the body is enlarged and its cohesion diminished without loss of its apparent microscopic homogeneity. Capillary intake is sharply distinguished from swelling. In more recent times a greater emphasis has been placed on the forces acting in the swelling process, and the meaning of "swelling" has been widened to cover such amounts of pore-filling liquids as have lost their free mobility as a result of forces acting at or within the surface of the porous material. Although practically all substances that possess the capacity to swell also have the common property of a large existing or potential surface, the different physicochemical characteristics of the swelling solids as well as of the liquid play exceedingly important parts in the process, thereby making it extremely difficult to explain swelling by any single physical or physicochemical phenomenon. The fact that liquids used in swelling may consist of (*a*) associated water-like molecules with large dipole moments, (*b*) molecules unlike water but with dipole moments, and (*c*) organic liquids without dipole moments suggests at least three different types of swelling. These are (*a*) polar liquids bound at the surface of a solid body thereby increasing its active volume, (*b*) liquids associated with the solid body as a solid solution (non-polar and polar molecules), and (*c*) polar liquids reacting with solids to form a complex compound. The existence of these different kinds of swelling has been proved by X-ray spectrography (9).[3]

Although intramicellar swelling has been shown to take place in clays (4, 5, 9), the data in this study indicate that intermicellar or surface phenomena are responsible for most of the swelling. The results in tables 1, 3, 5, and 6 and in figure 1 show the effect of exchangeable cations on the swelling

[3] Most of the discussion in this paragraph has been based upon the work of Katz (9).

of three different aluminosilicates. It is obvious that the colloidal clays and bentonite differ considerably both in their capacities to swell and in their behavior to the different ions on the exchange complex. As previously pointed out in the case of clays, the K ion behaves similarly to the divalent cations

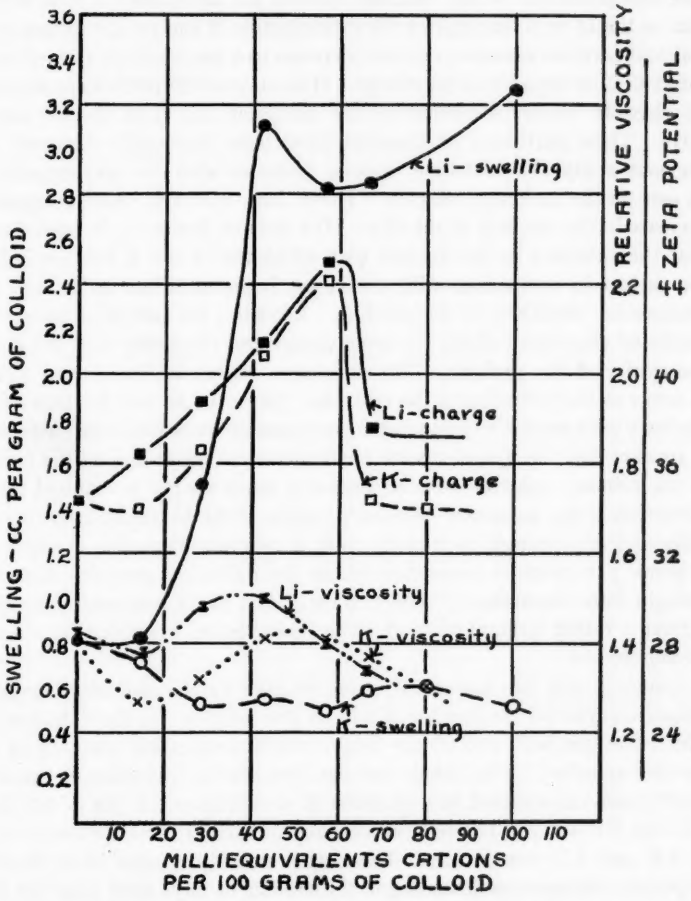

FIG. 1. COLLOIDAL PROPERTIES OF PUTNAM CLAY AS AFFECTED BY VARYING AMOUNTS OF EXCHANGEABLE Li AND K IONS

and the H ion in influencing the water sorption and swelling of these colloids. As a matter of fact, K-saturated clays swell less than any of the other clays. K-saturated bentonites, on the other hand, behave similarly to the Li- and Na-bentonites. These differences cannot be satisfactorily explained on the sole basis of ionic hydration.

A comparison of K- and Li-saturated Putnam colloids reveals several interesting facts concerning hydration. The data illustrated in figure 1 show the hydration of Putnam clay saturated with varying amounts of Li and K ions. Hydration is expressed in terms of relative viscosity and swelling. The zeta-potentials of the different systems are also shown. It is obvious that as the Li or K ions replace the exchangeable H ions on the surface of the colloidal particles the zeta-potential increases to a maximum at approximately the saturation capacity of the colloid. Hydration of the particles as measured by viscosity follows somewhat similar tendencies for both the Li- and K-clays. These particular relationships have been thoroughly discussed in a previous study (1). Swelling likewise increases with the concentration of Li ions on the exchange complex. The K ions, however, cause a significant decrease in the swelling of the clay. The data of Jenny (7) in table 8 show that the difference in the strength with which the Li and K ions are held on the surface in comparison with the H ion is not sufficient to explain such pronounced variations in the swelling. Likewise, the fact that Li- and K-saturated clays have about the same charge and dispersity does not add to the clarity of the problem. The differences cannot be interpreted directly in terms of the hydration of the two ions. Since the K- and Li-clays behave similarly with respect to hydration in an excess of water (colloidal suspension) it appears that the K-systems are unable to orient water around the surfaces of the primary colloidal particles whenever much energy is required for the dispersion of the secondary colloidal particles. The Li-colloid attracts water molecules very strongly even to the point of complete dispersion of aggregated systems. In colloidal suspension where the individual particles have been brought into suspension by some external force, the K-saturated surfaces do attract a rather large number of water molecules as evidenced by viscosity measurements.

Assuming that the amount of water oriented by the exchange complex is proportional to (*a*) the number of ions on the complex, (*b*) the tightness with which they are held, and (*c*) the field strength or orienting tendency of each ion as determined by its charge and size, the relative hydration of the different Putnam clays should be as follows: K = 1.0, Li = 2.3, Na = 1.4, Ca = 1.7, and Ba = 0.9. The relative swelling for each of these systems is 1, 10, 8, 1.8, and 1.7, respectively. These data strongly suggest that there are important influences contributing to the swelling of clays other than the effect of the exchangeable ions. It seems that the forces within the inner layer can attract to the colloidal surface water molecules as well as ions. Any explanation of the effect of the different ions on hydration must take into consideration not only the orienting tendency of the ions for water molecules, the number and kind of ions present[4] and their activities, but also the attractive power of the inner layer for water as it may be affected by ionic adsorption.

[4] After this paper was prepared, the attention of the authors was called to a forthcoming publication of Dr. E. W. Russell of the Rothamsted Experimental Station in which the effect of the exchangeable ions on hydration is thoroughly discussed.

The high swelling of bentonites in comparison with colloidal clays strongly suggests that the former attract large amounts of water as a result of forces

TABLE 9

Exchange of cations by different Putnam clay and bentonite systems [Jenny (7)]

Symmetry values

COLLOIDAL SYSTEM	NATURE OF CATION					
	Li	Na	K	Ca	Ba	H
Adsorption						
NH_4-Putnam clay	29.9	35.3	51.3	63.6	71.7	84.9
H-Putnam clay	6.6	6.2	14.5	26.9	23.8	....
H-Bentonite	18.0	14.6	18.4	....	....	....
Release						
NH_4Cl Putnam clays	57.0	58.9	42.0	29.3	....	6.9
NH_4Cl Bentonites	46.5	49.6	43.7	....	....	14.5

TABLE 10

Effect of SiO_2-sesquioxide ratio and exchange properties of colloidal clays on hydration

COLLOIDAL PROPERTY	TYPE OF H-COLLOID							
	Bentonite	Lufkin clay	Wabash clay	Putnam	Susquehanna clay	Iredell clay	Davidson clay	Cecil clay
SiO_2-R_2O_3 ratio	5.0	3.8	3.2	3.2	2.3	1.78	1.44	1.3
Symmetry value (release by K)	18.40	.....	.....	15.0	.....	16.66	20.33	.....
Exchange capacity, m.e./gm	0.95	0.82	0.78	0.65	0.47	0.35	0.12	0.13
Swelling, cc./gm	2.2	1.18	0.94	0.81	0.57	0.23	None	0.054
Heat of wetting, cal./gm	.....	15.0	13.9	13.8	11.7	.....	.....	5.9
Hygroscopicity (30 per cent H_2SO_4) per cent by weight	21.5	20.1	.....	18.1	15.5	.....	.....	6.1
Swelling (cc.) / Heat of wetting (cal.)	.....	0.079	0.068	0.059	0.048	.....	.....	0.0091
Hygroscopicity (per cent) / Heat of wetting (cal.)	.....	1.34	.....	1.31	1.33	.....	.....	1.03
Swelling (cc.) / Exchange capacity (m.e.)	2.44	1.44	1.20	1.24	1.21	0.66	.....	0.41
Hygroscopicity (per cent) / Exchange capacity (m.e.)	0.22	0.24	.....	0.28	0.33	.....	.....	0.47
Swelling (cc.) / Hygroscopicity (cc.)	10.23	5.87	.....	4.47	4.87	.....	.....	0.91

associated with the inner layer of the colloidal surface. There are several experimental facts that indicate the presence of this type of hydration. If

a comparison is made of the swelling of the Li-, Na-, and K-saturated bentonites and clays it is seen that the bentonite systems swell 116, 175, and 1610 per cent more, respectively, than the corresponding clays. The relative number of effective ions per gram of colloid as calculated from the saturation capacities (table 10) and the symmetry values (table 9, release) are 0.44, 0.47, and 0.41 m.e. for the Li-, Na-, and K-saturated bentonites. For the corresponding Putnam clay systems these values are 0.37, 0.38, and 0.27 m.e. These data show that such large differences in swelling in the two systems cannot be explained on the basis of ionic hydration. Moreover, the K-saturated bentonite is similar to the Li- and Na-systems in its swelling. Base exchange studies (table 9) and viscosity and dispersion (table 4) measurements show the same similarities. Marshall's data on dispersion also point out that the different exchangeable cations including the divalent ion have similar effects on the dispersity of bentonite. He explains these differences on the basis that bentonite is a montmorillonitic type of aluminosilicate with a high hydration; Putnam clay is described as a beidellitic type of colloid. Inasmuch as the colloidal behavior of bentonite classifies it as being more hydrophilic in nature than Putnam clay, it seems plausible to interpret these differences in swelling and hydration to variations in the attractive forces of the inner layer and the resulting increased mobility of the adsorbed ions, causing a measurable osmotic type of swelling.

The data in table 10 obtained in this investigation and other studies on colloidal clays (1, 2, 10) are summarized to show the relation of swelling and hydration to the nature of colloid and its exchange properties. It is observed that swelling increases with the SiO_2-sesquioxide ratio and the exchange capacity of the colloid; hygroscopicity and heat of wetting also increase with these properties of the colloid. Although swelling, heat of wetting, and hygroscopicity increase with the exchange capacity of the colloid, the relationship is not a simple one, since the relative activities of the exchangeable ions and the colloidal surface must be considered in addition to the number of ions present. For example, bentonite swells 2.44 cc. per milliequivalent of exchangeable cations present; Lufkin clay swells 1.44 cc.; Wabash, Putnam, and Susquehanna clays swell about 1.20 cc.; and Iredell, Davidson, and Cecil colloids swell much less than 1 cc. per milliequivalent. On the other hand, the amount of water adsorbed by the colloid from an atmosphere of water vapor per milliequivalent of exchangeable ions present increases with decreasing exchange capacity. Perhaps the structure of the colloid exerts considerable influences on water adsorption from an atmosphere of water vapor. If the ratio of swelling to water adsorption (hygroscopicity) is compared, it is observed that bentonites swell considerably in excess of the adsorbed water. The amount of water used by the Cecil clay in the swelling process, however, is a trifle less than the adsorbed water. Apparently, only sufficient water is taken up by this lateritic type of clay to satisfy the adsorptive properties of the surface. The ratio of swelling to the energy of water adsorption is likewise very low with this colloid.

It has been previously suggested that the physical structure of the primary particles as well as their possible aggregates may play an important rôle in water sorption, especially when dried colloidal powders are permitted to react with relatively large amounts of water either as a result of contact with a free water surface (sorption experiments) or with an atmosphere of water vapor. In a system where the primary particles possess a porous structure the size of the pores naturally limits the amount of water that can be adsorbed on the internal surface. Since these pores may also contain capillary water, sorption experiments do not give a direct clue as to the affinity of this internal surface for water. Permutites are examples of porous aluminosilicates; colloids extracted from lateritic types of soil also suggest a somewhat porous constitution. These types of colloids do not swell in water even though they may adsorb varying amounts of water from an atmosphere of water vapor. Non-porous and non-aggregated soil colloids with plate-shaped particles, however, are able under these same conditions to saturate their affinity for water to the highest possible degree. Such seems to be true in the swelling of Li- and Na-saturated Putnam and Wabash colloids where the amount of swelling water attained the hydration values calculated from the viscosity data. An intermediary case between the swelling behavior of porous colloids and non-porous plate-shaped clays would be expected when the shape of the particles approaches that of a sphere.

Low sorption values will also be found in the case of porous aggregates (stable aggregation) especially if the affinity of the primary particle for water is appreciably lower than that for another soil particle. Such may be the case to a limited extent with K-, Ba-, Ca-, and H-colloids. A qualitative measure of these affinities is the ease of dispersion. If it is assumed, as the results of these investigations suggest, especially those with the H-clays with small amounts of organic matter, that the entire swelling is due to hydratation, which in turn is proportional to the heat of wetting, then it can be concluded that Putnam, Wabash, and Lufkin clays have similarly shaped particles that are plate-like; Susquehanna and Cecil colloids seem to consist of either a more spherical type of particles or of porous primary particles.

It is obvious that the swelling or hydration of soil colloids is a rather complicated physical phenomenon. The results obtained in this investigation suggest certain interpretations of hydration in terms of the colloidal chemistry of the surface, that is, the effect of both the inner and outer parts of the electrical double layer in their relation to charge and hydration. It is interesting to compare these interpretations with the deductions of other investigators. Katz (8) has extensively studied the swelling of a large number of substances of widely varying character. Care was taken that swelling was not complicated by mechanical factors such as the porosity of the systems. From his experimental results Katz calculated, with the aid of thermodynamical reasoning, certain relationships between swelling pressure, heat of swelling, relative vapor pressure, etc. He compares the behavior of swelling substances to that of an ideal concentrated solution (Nernst), the heat of dilution of which can

be entirely changed into other forms of energy. Evidently the swelling of soils and clays is more complicated; but there is reason to believe that the hydratation of clays follows the laws developed by Katz.

Terzaghi (13) has studied the swelling of elastic systems with porous structures (soils). He has interpreted the swelling of these systems as being due to the combined action of the surface tension of the water in the system and the elasticity of the solid components. Although the results of Terzaghi's work are of extreme importance in soil mechanics, a more physicochemical interpretation is necessary to describe the hydration phenomena in colloidal clay systems.

Mattson (12) has explained the swelling of colloidal clays on the basis of the Donnan equilibrium as developed by Wilson and by Proctor and Wilson. The data obtained in the present study indicate that the swelling of bentonites may be at least partially explained by the Donnan concept but that this type of swelling cannot account for an appreciable amount of the hydration displayed by the common clay colloids.

The work of Langmuir, Harkins, Debye, and others, who have developed the concept of molecular orientations on surfaces and interfaces and around ions, has been used in formulating the concept of swelling in the present investigation.

SUMMARY

A study has been made of the influence of the structure of soil colloids and of the amount and nature of ions at the surface on such colloidal properties as sorption of liquids, heat of wetting, viscosity of suspensions, zeta-potential of the dispersed particles, hygroscopicity, and hydration.

On the basis of these experimental data hydration is explained as being due in largest degree to the orienting influence on dipole molecules of the colloid surface as well as of the adsorbed cations. With special colloids (bentonite and alkali-saturated organic matter) an osmotic type of swelling seems to play a significant rôle.

The importance of the shape of the primary and secondary colloidal particles on the evaluation of swelling from sorption data is stressed.

The principal swelling theories are briefly discussed in their relation to the data and conclusions of this particlaur study.

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John Sharkey Carroll

1871-1935

John Sharkey Carroll, prominent in the fertilizer industry of this country for more than 30 years, died at his home in Jackson, Mississippi, on September 15.

Mr. Carroll was born in Oktibbeha County, Mississippi, in 1871. He received the bachelor of science degree, for work in agriculture, and the master of science degree, for work in agricultural chemistry, from the Mississippi Agricultural College. For more than 10 years he served that institution as instructor and, later, as assistant professor of chemistry and assistant state chemist. From 1904 until his death, he was connected with the agricultural and scientific work of the potash interests.

Mr. Carroll was a member of several learned societies, agricultural associations, and local organizations.